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(54) **UV CURABLE COMPOSITION FOR USE IN 3D PRINTING**

UV-HÄRTBARE ZUSAMMENSETZUNG ZUR VERWENDUNG BEIM 3D-DRUCKEN

COMPOSITION DURCISSABLE PAR UV DESTINÉE À ÊTRE UTILISÉE EN IMPRESSION 3D

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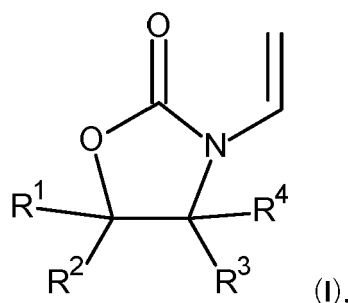
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US-A- 4 738 870 US-A- 4 929 403
US-A1- 2016 193 852

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Description

[0001] The present invention relates to the use of a photocurable composition in a photopolymerization 3D printing process, wherein the photocurable composition comprises (A1) a N-vinyloxazolidinone of formula



wherein

R¹, R², R³ and R⁴ are independently of each other a hydrogen atom or an organic group having not more than 10 carbon atoms,

(A2) optionally one, or more second reactive diluents,

(B) one, or more oligomers, and

(C) a photoinitiator (C), wherein the amount of component (A1) is 5 to 70 % by weight based on the amount of components (A1), (A2) and (B), wherein the viscosity of said photocurable composition is in the range 10 to 3000 mPa·s, preferably 10 to 1500 mPa·s at 30 ° C. The compositions, from which cured three-dimensional shaped articles having balanced mechanical properties combining stiffness with high toughness can be made, are particularly suitable for the production of three-dimensional articles by stereolithography and photopolymer jetting.

[0002] JP57109813 discloses a curing composition that is composed of N-vinyl-2-oxazolidone and a crosslinkable monomer containing acryloyl or methacryloyl groups, thus suitably being used as a coating material for metal, because of its high curing rate and high adhesion.

[0003] EP-A-555 069 discloses that the performance characteristics of radiation curable compositions can be improved by adding solid monomers, in particular N-vinylcaprolactam. However, the handling of such solid monomers is disadvantageous. According to WO2010/057839 N-vinylcaprolactam may be replaced by a mixture of N-vinylcaprolactam with an N-vinylamide.

[0004] US4639472 discloses radiation curable compositions comprising N-vinyloxazolidinone. Printing inks are mentioned as one possible application of such radiation curable compositions.

[0005] US4738870 relates to a photopolymerizable composition comprising a (hydroxy)phosphinylalkyl compound of the formula $\text{HOP(=O)-CR'R''-O-C(=O)-C(R)=CH}_2$ wherein R is hydrogen, methyl or ethyl and R' and R'' are selected independently from hydrogen and alkyl of 1-10 carbon atoms, in an amount sufficient to promote adhesion of the resulting photopolymerizable composition to a substrate; at least one copolymerizable ethylenically unsaturated monomer in an amount sufficient to provide the resulting photopolymerized composition with desired physical properties and a photoinitiator in an amount sufficient to initiate polymerization upon exposing the composition to light and a process for coating a substrate comprising applying to the substrate the composition of US4738870 and exposing the thus-coated substrate to actinic radiation for a time sufficient to photopolymerize the composition.

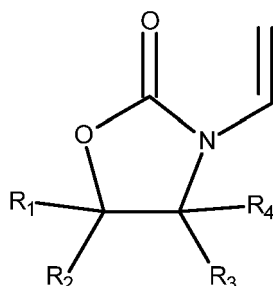
[0006] US4929403 relates to a process for rapidly forming a multilayer flexible mold for finely detailed objects from a radiatively curable molding composition, the process comprising: (a) coating at least a portion of the surface of a three-dimensional object with a fluid molding composition, the molding composition being radiatively curable; (b) curing the coating to form an elastic, flexible layer of cured molding composition on the three-dimensional object by exposing the fluid coating composition to radiative energy; (c) repeating steps (a) and (b) successively until a self-supporting multilayer elastic coating of cured molding composition has been formed on the three-dimensional object, the multilayer coating being sufficiently strong so as to not distort perceptibly when filled with a molding material having a low to moderate density; and (d) removing the three-dimensional object.

[0007] US4929403 relates to a process for rapidly forming a multilayer flexible mold for finely detailed objects from a radiatively curable molding composition, the process comprising: (a) coating at least a portion of the surface of a three-dimensional object with a fluid molding composition, the molding composition being radiatively curable; (b) curing the coating to form an elastic, flexible layer of cured molding composition on the three-dimensional object by exposing the fluid coating composition to radiative energy; (c) repeating steps (a) and (b) successively until a self-supporting multilayer

elastic coating of cured molding composition has been formed on the three-dimensional object, the multilayer coating being sufficiently strong so as to not distort perceptibly when filled with a molding material having a low to moderate density; and (d) removing the three-dimensional object.

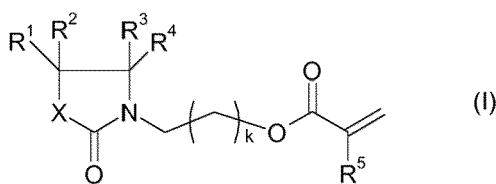
[0008] The fluid molding composition may comprise (a) at least one crosslinkable oligomer; (b) at least one reactive diluent; and (c) at least one photoinitiator.

[0009] WO2015022228 relates to the use of a radiation curable composition as printing ink for ink-jet printing, wherein the radiation curable composition comprises N-vinyloxazolidinone of formula



in which R_1 to R_4 independently from each other are a hydrogen atom or an organic radical having not more than 10 carbon atoms.

[0010] WO18146259 relates to compositions, comprising a compound of formula (I)



wherein

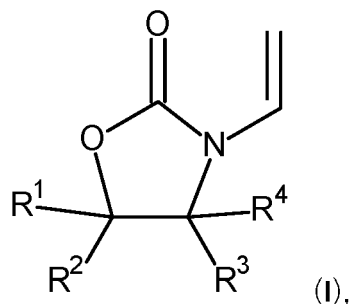
R_1, R_2, R_3, R_4 are each independently H, C_1-C_6 -alkyl, C_1-C_6 -alkoxy, or C_1-C_6 -alkoxy- C_1-C_6 -alkyl;
 R_5 is H or C_1-C_6 -alkyl;
 X is CR_6R_7 , O, or NR^8 ;
 R_6, R_7 are each independently H, C_1-C_6 -alkyl, C_1-C_6 -alkoxy, or C_1-C_6 -alkoxy- C_1-C_6 -alkyl; R^8 is H, C_1-C_6 -alkyl, or C_1-C_6 -alkoxy- C_1-C_6 -alkyl; k is 1, 2, 3, 4 or 5 and the use of the compositions as printing inks, in particular inkjet printing inks.

[0011] It is the object of the present invention to provide photocurable compositions for 3D printing, in particular in photopolymer jetting and stereolithography. The photocurable compositions should have a high reactivity in radiation curing and should allow a 3D printing process resulting in three-dimensional articles with improved characteristics, in particular balanced mechanical properties combining stiffness with high toughness.

[0012] It has surprisingly been found that N-vinyloxazolidinone of formula (I) provide a strong diluting effect for high viscous oligomers resulting in a higher amount of oligomers which in fact may have a positive impact on stiffness/toughness. Cured three-dimensional shaped articles having balanced mechanical properties combining stiffness with high toughness can be made from the photocurable compositions used according to the present invention, in particular by stereolithography and photopolymer jetting.

[0013] Accordingly, the present invention is directed to the use of a photocurable composition in a photopolymerization 3D printing process, in particular vat photopolymerisation, or photopolymer jetting, wherein the photocurable composition comprises

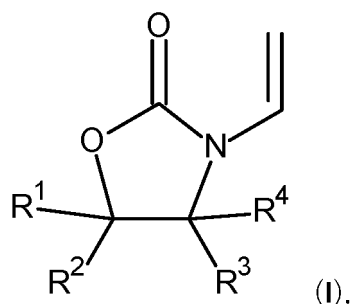
(A1) a N-vinyloxazolidinone of formula



wherein

R¹, R², R³ and R⁴ are independently of each other a hydrogen atom or an organic group having not more than 10 carbon atoms,
 (A2) optionally one, or more second reactive diluents,
 (B) one, or more oligomers, and
 (C) a photoinitiator (C), wherein the amount of component (A1) is 5 to 70 % by weight based on the amount of components (A1), (A2) and (B).

[0014] The photocurable composition comprises preferably (A1) a N-vinyloxazolidinone of formula



wherein

R¹, R², R³ and R⁴ are independently of each other a hydrogen atom or an organic group having not more than 10 carbon atoms,
 (A2) optionally one, or more second reactive diluents,
 (B) one, or more oligomers, and
 (C) a photoinitiator (C), wherein the amount of component (A1) is 5 to 70 % by weight based on the amount of components (A1), (A2) and (B), wherein the amount of components (A1) and (A2) is 30 to 70 % by weight and the amount of component (B) is 70 to 30 % by weight based on the amount of components (A1) and (A2) and (B).

[0015] The amount of components (A1) and (A2) is especially 30 to 50 % by weight, very especially 40 to 60 % by weight based on the amount of components (A1) and (A2) and (B).

[0016] The amount of component (B) is especially 70 to 50 % by weight, very especially 60 to 40 % by weight based on the amount of components (A1) and (A2) and (B).

[0017] The viscosity of the photocurable compositions is generally in the range 10 to 3000 mPa·s, preferably 10 to 1500 mPa·s at 30 ° C. In case of photopolymer jetting the viscosity of the photocurable composition is adjusted to be in the range of 10 to 150 mPas at 30 ° C. In case of vat-based photopolymerization the viscosity of the photocurable composition is adjusted to be in the range of 50 to 1500 mPas at 30 ° C. Most commercial print heads require heating to reduce ink viscosity which is typically in the range of 10 to 20 mPas.

[0018] Photocurable compositions, comprising N-vinyloxazolidinone of formula (I) have a significantly lower viscosity than photocurable compositions, comprising instead of N-vinyloxazolidinone of formula (I) acryloylmorpholine (ACMO). N-vinyloxazolidinone of formula (I) provide a strong diluting effect for high viscous oligomers, offering more flexibility with respect to the development of formulations and better mechanical properties of the cured three-dimensional shaped articles, in particular balanced mechanical properties combining stiffness with high toughness.

[0019] In addition, the present invention relates to a method for producing a three-dimensional article, comprising

- a) providing the photocurable composition used according to the present invention,
- b) exposing the photocurable composition to actinic radiation to form a cured crosssection,
- c) repeating steps (a) and (b) to build up a three-dimensional article.

[0020] The amount of component (A1) is 5 to 70 % by weight based on the amount of components (A1), (A2) and (B).

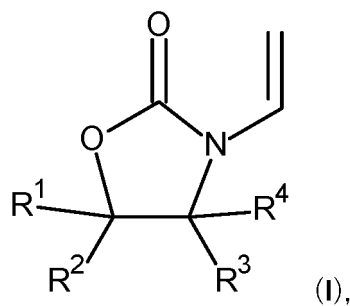
[0021] The amount of components (A1) and (A2) is 30 to 70 % by weight, especially 30 to 50 % by weight, very especially 40 to 60 % by weight based on the amount of components (A1) and (A2) and (B).

[0022] The amount of component (B) is 70 to 30 % by weight, especially 70 to 50 % by weight, very especially 60 to 40 % by weight based on the amount of components (A1) (and (A2) and (B).

[0023] If the composition used according to the present invention comprises the second diluent (A2), it is contained in an amount of 5 to 65 % by weight based on the amount of components (A1), (A2) and (B). In said embodiment the amount of component (A1) is 65 to 5 % by weight based on the amount of components (A1), (A2) and (B).

[0024] In a particularly preferred embodiment the composition used according to the present invention does not include component (A2) and the amount of component (A1) is 30 to 70 % by weight, especially 30 to 50 % by weight, very especially 40 to 60 % by weight and the amount of component (B) is 70 to 30 % by weight, especially 70 to 50 % by weight, very especially 60 to 40 % by weight based on the amount of components (A1) and (B).

[0025] In said embodiment the photocurable composition comprises (A1) a N-vinyloxazolidinone of formula



wherein

R¹, R², R³ and R⁴ are independently of each other a hydrogen atom or an organic group having not more than 10 carbon atoms,

(B) one, or more oligomers, and

(C) a photoinitiator (C), wherein the amount of component (A1) is 30 to 70 % by weight, and the amount of component (B) is 70 to 30 % by weight based on the amount of components (A1) and (B).

[0026] The viscosity of the photocurable compositions is generally in the range 10 to 3000 mPa·s, preferably 10 to 1500 mPa·s at 30 °C. In case of photopolymer jetting the viscosity of the photocurable composition is adjusted to be in the range of 10 to 150 mPa·s at 30 °C. In case of vat-based photopolymerization the viscosity of the photocurable composition is adjusted to be in the range of 50 to 1500 mPa·s at 30 °C.

[0027] The amount of component (A1) is especially 30 to 50 % by weight, very especially 40 to 60 % by weight and the amount of component (B) is especially 70 to 50 % by weight, very especially 60 to 40 % by weight based on the amount of components (A1) and (B).

[0028] The viscosity of the photocurable compositions is generally in the range 10 to 3000 mPa·s, preferably 10 to 1500 mPa·s at 30 °C. In case of photopolymer jetting the viscosity of the photocurable composition is adjusted to be in the range of 10 to 150 mPa·s at 30 °C. In case of vat-based photopolymerization the viscosity of the photocurable composition is adjusted to be in the range of 50 to 1500 mPa·s at 30 °C.

N-Vinyloxazolidinone (A1)

[0029] Preferably at least two of R¹ to R⁴ in formula (I) are a hydrogen atom.

[0030] In a particularly preferred embodiment at least two of R¹ to R⁴ in formula (I) are a hydrogen atom and any remaining R¹ to R⁴ are an organic group having not more than 10 carbon atoms.

[0031] Preferably the organic group has not more than 4 carbon atoms. In a particularly preferred embodiment the organic group is an alkyl, or alkoxy group. In a preferred embodiment the organic group is a C₁-C₄alkyl group, or a

C₁-C₄alkoxy group. In a most preferred embodiment the organic group is a methyl group.

[0032] As examples of N-vinyloxazolidinone of formula (I) compounds may be mentioned, wherein

R¹, R², R³ and R⁴ are a hydrogen atom (N-vinyloxazolidinone (NVO), or

R¹ is a C₁-C₄alkyl group, in particular a methyl group, and R², R³ and R⁴ are a hydrogen atom (N-vinyl-5-methyl oxazolidinone (NVMO), or

R¹ and R² are a hydrogen atom and R³ and R⁴ are a C₁-C₄alkyl group, in particular a methyl group.

[0033] Particularly preferred are NVO and NVMO, most preferred is NVMO.

Second Diluent (A2)

[0034] The second diluent (B) may be a single diluent, or a mixture of two, or more diluents.

[0035] The second diluent (B) represents a "reactive diluent", which is a component that contains at least one free radically reactive group (e.g., an ethylenically-unsaturated group) that can co-react with components (A1) and (B) (e.g., is capable of undergoing addition polymerization).

[0036] If the composition used according to the present invention comprises the second diluent (A2), it is contained in an amount of 5 to 65 % by weight based on the amount of components (A1), (A2) and (B).

[0037] Suitable monofunctional, difunctional, or tetrafunctional acrylate, methacrylate, or vinylamide components are listed below. Monofunctional refers to the fact that the molecule of the compound exhibits only one acrylate, methacrylate, or vinylamide functional group.

[0038] Examples of monofunctional vinylamide components include such as N-vinyl-pyrrolidone, vinyl-imidazole, N-vinylcaprolactame, N-(hydroxymethyl)vinylamide, N-hydroxyethyl vinylamide, N-isopropylvinylamide, N-isopropylmeth-vinylamide, N-tert-butylvinylamide, N,N'-methylenebisvinylamide, N-(isobutoxymethyl)vinylamide, N-(butoxymethyl)vi-nylamide, N-[3-(dimethylamino)propyl]methvinylamide, N,N-dimethylvinylamide, N,N-diethylvinylamide and N-methyl-N-vinylacetamide.

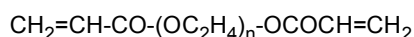
[0039] Examples of monofunctional methacrylate include isobornyl methacrylate, tetrahydrofurfuryl methacrylate, ethoxylated phenyl methacrylate, cyclohexylmethacrylate, lauryl methacrylate, stearyl methacrylate, octyl methacrylate, isodecyl methacrylate, tridecyl methacrylate, caprolactone methacrylate, nonyl phenol methacrylate, cyclic trimethylol-propane formal methacrylate, methoxy polyethyleneglycol methacrylates, methoxy polypropyleneglycol methacrylates, hydroxyethyl methacrylate, hydroxypropyl methacrylate and glycidyl methacrylate.

[0040] The photocurable composition used according to the present invention may contain a difunctional, or tetrafunc-tional diluent having two unsaturated carbon-carbon bonds, such as, for example, difunctional, or tetrafunctional (meth)acrylates.

[0041] Examples of the bifunctional monomer include 1,3-butylene glycol di(meth)acrylate, 1,4-butanediol di(meth)acr-ylate, diethylene glycol di(meth)acrylate, 1,6-hexanediol di(meth)acrylate, polyethylene glycol (200) di(meth)acrylate, tetraethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tripropylene glycol di(meth)acrylate, polyeth-ylene glycol (400) di(meth)acrylate, ethoxylated (3) bisphenol A di(meth)acrylate, dipropylene glycol di(meth)acrylate, alkoxyated hexanediol di(meth)acrylate, ethoxylated (4) bisphenol A di(meth)acrylate, ethoxylated (10) bisphenol A di(meth)acrylate, polyethylene glycol (600) di(meth)acrylate, tricyclodecane dimethanol di(meth)acrylate, 1,9-nonanediol di(meth)acrylate, 1,10-decanediol di(meth)acrylate, neopentyl glycol di(meth)acrylate, polytetramethylene glycol di(meth)acrylate, 3-methyl-1,5-pentanediol di(meth)acrylate, and dimethylol-tricyclodecane di(meth)acrylate. One of these may be used alone, or two or more of these may be used in combination.

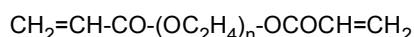
[0042] Polyethylene glycol (200) diacrylate, polyethylene glycol (400) diacrylate, and polyethylene glycol (600) diacr-ylate mentioned above are represented by the chemical formulae below.

[0043] Polyethylene glycol (200) diacrylate



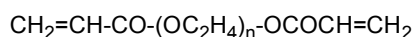
where $n \approx 4$

[0044] Polyethylene glycol (400) diacrylate



where $n \approx 14$

[0045] Polyethylene glycol (600) diacrylate



where $n \approx 14$

[0046] Examples of tetrafunctional (meth)acrylates are bistrimethylolpropane tetraacrylate, pentaerythritol tetraacrylate, tetramethylolmethane tetramethacrylate, pentaerythritol tetramethacrylate, bistrimethylolpropane tetramethacrylate, ethoxylated pentaerythritol tetraacrylate, propoxylated pentaerythritol tetraacrylate, dipentaerythritol tetraacrylate, ethoxylated dipentaerythritol tetraacrylate, propoxylated dipentaerythritol tetraacrylate, aryl urethane tetraacrylates, aliphatic urethane tetraacrylates, melamine tetraacrylates, epoxy novolac tetraacrylates and polyester tetraacrylates.

[0047] The photocurable composition used according to the present invention may contain monofunctional acrylamides or methacrylamides. Examples include acryloylmorpholine, methacryloylmorpholine, N-(hydroxymethyl)acrylamide, N-hydroxyethyl acrylamide, N-isopropylacrylamide, N-isopropylmethacrylamide, N-tert-butylacrylamide, N,N'-methylenebisacrylamide, N-(isobutoxymethyl)acrylamide, N-(butoxymethyl)acrylamide, N-[3-(dimethylamino)propyl]methacrylamide, N,N-dimethylacrylamide, N,N-diethylacrylamide, N-(hydroxymethyl)methacrylamide, N-hydroxyethyl methacrylamide, N-isopropyl methacrylamide, N-isopropylmethmethacrylamide, N-tert-butylmethacrylamide, N,N'-methylenebis-methacrylamide, N-(isobutoxymethyl)methacrylamide, N-(butoxymethyl) methacrylamide, N-[3-(dimethylamino) propyl] meth methacrylamide, N,N-dimethylmethacrylamide and N,N-diethylmethacrylamide.

Oligomer (B)

[0048] The oligomer (B) is selected from polyester (meth)acrylates, polyether (meth)acrylates, carbonate (meth)acrylates, epoxy (meth)acrylates and urethane (meth)acrylates, including amine-modified oligomers. The oligomer (B) may be single oligomer, or a mixture of two, or more oligomers.

[0049] Urethane (meth)acrylates are obtainable for example by reacting polyisocyanates with hydroxyalkyl (meth)acrylates and optionally chain extenders such as diols, polyols, diamines, polyamines, dithiols or polythiols.

[0050] Urethane (meth)acrylates of this kind comprise as synthesis components substantially:

- (1) at least one organic aliphatic, aromatic or cycloaliphatic di- or polyisocyanate,
- (2) at least one compound having at least one isocyanate-reactive group and at least one radically polymerizable unsaturated group, and
- (3) optionally, at least one compound having at least two isocyanate-reactive groups.

[0051] Suitable components (1) are, for example, aliphatic, aromatic, and cycloaliphatic diisocyanates and polyisocyanates having an NCO functionality of at least 2, preferably 2 to 5, and more preferably more than 2 to 4.

[0052] Polyisocyanates contemplated include polyisocyanates containing isocyanurate groups, uretdione diisocyanates, polyisocyanates containing biuret groups, polyisocyanates containing urethane groups or allophanate groups, polyisocyanates comprising oxadiazinetrione groups, uretonimine-modified polyisocyanates of linear or branched C_4 - C_{20} alkylene diisocyanates, cycloaliphatic diisocyanates having a total of 6 to 20 C atoms, or aromatic diisocyanates having a total of 8 to 20 C atoms, or mixtures thereof.

[0053] Examples of customary diisocyanates are aliphatic diisocyanates such as tetramethylene diisocyanate, hexamethylene diisocyanate (1,6-diisocyanatohexane), trimethylhexamethylene diisocyanate, octamethylene diisocyanate, decamethylene diisocyanate, dodecamethylene diisocyanate, tetradecamethylene diisocyanate, derivatives of lysine diisocyanate, tetramethylxylylene diisocyanate, trimethylhexane diisocyanate or tetramethylhexane diisocyanate, cycloaliphatic diisocyanates such as 1,4-, 1,3- or 1,2-diisocyanatocyclohexane, 4,4'- or 2,4'-di(isocyanatocyclohexyl)methane, 1-isocyanato-3,3,5-trimethyl-5-(isocyanatomethyl)cyclohexane (isophorone diisocyanate), 1,3- or 1,4-bis(isocyanatomethyl)cyclohexane or 2,4- or 2,6-diisocyanato-1-methylcyclohexane, and also aromatic diisocyanates such as tolylene 2,4- or 2,6-diisocyanate and the isomer mixtures thereof, m- or p-xylylene diisocyanate, 2,4'- or 4,4'-diisocyanatodiphenylmethane and the isomer mixtures thereof, phenylene 1,3- or 1,4-diisocyanate, 1-chlorophenylene 2,4-diisocyanate, naphthylene 1,5-diisocyanate, diphenylene 4,4'-diisocyanate, 4,4'-diisocyanato-3,3'-dimethylbiphenyl, 3-methyldiphenylmethane 4,4'-diisocyanate, tetramethylxylylene diisocyanate, 1,4-diisocyanatobenzene or diphenyl ether 4,4'-diisocyanate.

[0054] Mixtures of the stated diisocyanates may also be present.

[0055] Contemplated as component (2) in accordance with the invention is at least one compound (2) which carries at least one isocyanate-reactive group and at least one radically polymerizable group.

[0056] The compounds (2) preferably have precisely one isocyanate-reactive group and 1 to 5, more preferably 1 to 4, and very preferably 1 to 3 radically polymerizable groups.

[0057] The components (2) preferably have a molar weight of below 10 000 g/mol, more preferably below 5000 g/mol, very preferably below 4000 g/mol, and more particularly below 3000 g/mol. Special components (b) have a molar weight of below 1000 or even below 600 g/mol.

[0058] Isocyanate-reactive groups may be, for example, -OH, -SH, -NH₂, and -NHR¹⁰⁰, where R¹⁰⁰ is hydrogen or an

alkyl group containing 1 to 4 carbon atoms, such as methyl, ethyl, *n*-propyl, *isopropyl*, *n*-butyl, *isobutyl*, *sec*-butyl or *tert*-butyl, for example. Components (2) may be, for example, monoesters of α,β -unsaturated carboxylic acids, such as acrylic acid, methacrylic acid, crotonic acid, itaconic acid, fumaric acid, maleic acid, acrylamidoglycolic acid and methacrylamidoglycolic acid, and polyols, which have preferably 2 to 20 C atoms and at least two hydroxyl groups, such as ethylene glycol, diethylene glycol, triethylene glycol, propylene 1,2-glycol, propylene 1,3-glycol, 1,1-dimethyl-1,2-ethanediol, dipropylene glycol, triethylene glycol, tetraethylene glycol, pentaethylene glycol, tripropylene glycol, 1,2-, 1,3- or 1,4-butanediol, 1,5-pentanediol, neopentyl glycol, 1,6-hexanediol, 2-methyl-1,5-pentanediol, 2-ethyl-1,4-butanediol, 1,4-dimethylolcyclohexane, 2,2-bis(4-hydroxycyclohexyl)propane, glycerol, trimethylolethane, trimethylolpropane, trimethylolbutane, pentaerythritol, ditrimethylolpropane, erythritol, sorbitol, polyethylene glycol having a molar mass of between 106 and 2000, polypropylene glycol having a molar weight of between 134 and 2000, polyTHF having a molar weight of between 162 and 2000 or poly-1,3-propanediol having a molar weight of between 134 and 400. In addition it is also possible to use esters or amides of (meth)acrylic acid with amino alcohols such as 2-aminoethanol, 2-(methylamino)ethanol, 3-amino-1-propanol, 1-amino-2-propanol or 2-(2-aminoethoxy)ethanol, for example, 2-mercaptoethanol or polyaminoalkanes, such as ethylenediamine or diethylenetriamine, or vinylacetic acid.

[0059] Also suitable, furthermore, albeit less preferably, are unsaturated polyetherols or polyesterols or polyacrylate polyols having an average OH functionality of 2 to 10.

[0060] Examples of amides of ethylenically unsaturated carboxylic acids with amino alcohols are hydroxyalkyl(meth)acrylamides such as N-hydroxymethylacrylamide, N-hydroxymethylmethacrylamide, N-hydroxyethyl acrylamide, N-hydroxyethylmethacrylamide, 5-hydroxy-3-oxapentyl(meth)acrylamide, N-hydroxyalkylcrotonamides such as N-hydroxymethylcrotonamide, or N-hydroxyalkylmaleimides such as N-hydroxyethylmaleimide.

[0061] Preference is given to using 2-hydroxyethyl (meth)acrylate, 2- or 3-hydroxypropyl (meth)acrylate, 1,4-butanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, 1,5-pentanediol mono(meth)acrylate, 1,6-hexanediol mono(meth)acrylate, glycerol mono(meth)acrylate and di(meth)acrylate, trimethylolpropane mono(meth)acrylate and di(meth)acrylate, pentaerythritol mono(meth)acrylate, di(meth)acrylate, and tri(meth)acrylate, and also 2-aminoethyl (meth)acrylate, 2-aminopropyl (meth)acrylate, 3-aminopropyl (meth)acrylate, 4-aminobutyl (meth)acrylate, 6-aminoethyl (meth)acrylate, 2-thioethyl (meth)acrylate, 2-aminoethyl(meth)acrylamide, 2-aminopropyl(meth)acrylamide, 3-aminopropyl(meth)acrylamide, 2-hydroxyethyl(meth)acrylamide, 2-hydroxypropyl(meth)acrylamide, or 3-hydroxypropyl(meth)acrylamide. Particularly preferred are 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2- or 3-hydroxypropyl acrylate, 1,4-butanediol monoacrylate, 3-(acryloyloxy)-2-hydroxypropyl (meth)acrylate, and also the monoacrylates of polyethylene glycol with a molar mass of 106 to 238.

[0062] Contemplated as component (3) are compounds which have at least two isocyanate-reactive groups, examples being -OH, -SH, -NH₂ or -NH R¹⁰¹, in which R¹⁰¹ therein, independently of one another, may be hydrogen, methyl, ethyl, *isopropyl*, *n*-propyl, *n*-butyl, *isobutyl*, *sec*-butyl or *tert*-butyl.

[0063] Compounds (3) having precisely 2 isocyanate-reactive groups are preferably diols having 2 to 20 carbon atoms, examples being ethylene glycol, 1,2-propanediol, 1,3-propanediol, 1,1-dimethylethane-1,2-diol, 2-butyl-2-ethyl-1,3-propanediol, 2-ethyl-1,3-propanediol, 2-methyl-1,3-propanediol, neopentyl glycol, neopentyl glycol hydroxypivalate, 1,2-, 1,3- or 1,4-butanediol, 1,6-hexanediol, 1,10-decanediol, bis(4-hydroxycyclohexane)isopropylidene, tetramethylcyclobutanediol, 1,2-, 1,3- or 1,4-cyclohexanediol, cyclooctanediol, norbornanediol, pinanediol, decalindiol, 2-ethyl-1,3-hexanediol, 2,4-diethyloctane-1,3-diol, hydroquinone, bisphenol A, bisphenol F, bisphenol B, bisphenol S, 2,2-bis(4-hydroxycyclohexyl)propane, 1,1-, 1,2-, 1,3-, and 1,4-cyclohexanedimethanol, 1,2-, 1,3-, or 1,4-cyclohexanediol, polyTHF having a molar mass of between 162 and 2000, poly-1,2-propanediol or poly-1,3-propanediol having a molar mass of between 134 and 1178 or polyethylene glycol having a molar mass of between 106 and 2000, and also aliphatic diamines, such as methylene- and isopropylidene-bis(cyclohexylamine), piperazine, 1,2-, 1,3- or 1,4-diaminocyclohexane, 1,2-, 1,3-, or 1,4-cyclohexanebis(methylamine), etc., dithiols or polyfunctional alcohols, secondary or primary amino alcohols, such as ethanolamine, monopropanolamine, etc. or thio alcohols, such as thioethylene glycol.

[0064] Particularly suitable here are the cycloaliphatic diols, such as, for example, bis(4-hydroxycyclohexane)isopropylidene, tetramethylcyclobutanediol, 1,2-, 1,3-, or 1,4-cyclohexanediol, 1,1-, 1,2-, 1,3-, and 1,4-cyclohexanedimethanol, cyclooctanediol or norbornanediol.

[0065] Further compounds (3) may be compounds having at least three isocyanate-reactive groups.

[0066] For example, these components may have 3 to 6, preferably 3 to 5, more preferably 3 to 4, and very preferably 3 isocyanate-reactive groups.

[0067] The molecular weight of these components is generally not more than 2000 g/mol, preferably not more than 1500 g/mol, more preferably not more than 1000 g/mol, and very preferably not more than 500 g/mol.

[0068] The urethane (meth)acrylates preferably have a number-average molar weight M_n of 500 to 20 000, in particular of 500 to 10 000 and more preferably 600 to 3000 g/mol (determined by gel permeation chromatography using tetrahydrofuran and polystyrene as standard).

[0069] Epoxy (meth)acrylates are obtainable by reacting epoxides with (meth)acrylic acid. Examples of suitable epoxides include epoxidized olefins, aromatic glycidyl ethers or aliphatic glycidyl ethers, preferably those of aromatic or

aliphatic glycidyl ethers.

[0070] Examples of possible epoxidized olefins include ethylene oxide, propylene oxide, isobutylene oxide, 1-butene oxide, 2-butene oxide, vinyloxirane, styrene oxide or epichlorohydrin, preference being given to ethylene oxide, propylene oxide, isobutylene oxide, vinyloxirane, styrene oxide or epichlorohydrin, particular preference to ethylene oxide, propylene oxide or epichlorohydrin, and very particular preference to ethylene oxide and epichlorohydrin.

[0071] Aromatic glycidyl ethers are, for example, bisphenol A diglycidyl ether, bisphenol F diglycidyl ether, bisphenol B diglycidyl ether, bisphenol S diglycidyl ether, hydroquinone diglycidyl ether, alkylation products of phenol/dicyclopentadiene, e.g., 2,5-bis[(2,3-epoxypropoxy)phenyl]octahydro-4,7-methano-5H-indene (CAS No. [13446-85-0]), tris[4-(2,3-epoxypropoxy)phenyl]methane isomers (CAS No. [66072-39-7]), phenol-based epoxy novolaks (CAS No. [9003-35-4]), and cresol-based epoxy novolaks (CAS No. [37382-79-9]).

[0072] Examples of aliphatic glycidyl ethers include 1,4-butanediol diglycidyl ether, 1,6-hexanediol diglycidyl ether, trimethylolpropane triglycidyl ether, pentaerythritol tetraglycidyl ether, 1,1,2,2-tetrakis[4-(2,3-epoxypropoxy)phenyl]ethane (CAS No. [27043-37-4]), diglycidyl ether of polypropylene glycol (α , ω -bis(2,3-epoxypropoxy)poly(oxypropylene), CAS No. [16096-30-3]) and of hydrogenated bisphenol A (2,2-bis[4-(2,3-epoxypropoxy)cyclohexyl]propane, CAS No. [13410-58-7]).

[0073] The epoxy (meth)acrylates preferably have a number-average molar weight M_n of 200 to 20 000, more preferably of 200 to 10 000 g/mol, and very preferably of 250 to 3000 g/mol; the amount of (meth)acrylic groups is preferably 1 to 5, more preferably 2 to 4, per 1000 g of epoxy (meth)acrylate (determined by gel permeation chromatography using polystyrene as standard and tetrahydrofuran as eluent).

[0074] Carbonate (meth)acrylates comprise on average preferably 1 to 5, especially 2 to 4, more preferably 2 to 3 (meth)acrylic groups, and very preferably 2 (meth)acrylic groups.

[0075] The number-average molecular weight M_n of the carbonate (meth)acrylates is preferably less than 3000 g/mol, more preferably less than 1500 g/mol, very preferably less than 800 g/mol (determined by gel permeation chromatography using polystyrene as standard, tetrahydrofuran as solvent).

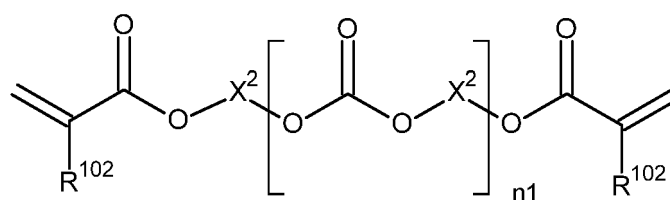
[0076] The carbonate (meth)acrylates are obtainable in a simple manner by transesterifying carbonic esters with polyhydric, preferably dihydric, alcohols (diols, hexanediol for example) and subsequently esterifying the free OH groups with (meth)acrylic acid, or else by transesterification with (meth)acrylic esters, as described for example in EP-A 92 269. They are also obtainable by reacting phosgene, urea derivatives with polyhydric, e.g., dihydric, alcohols.

[0077] Also conceivable are (meth)acrylates of polycarbonate polyols, such as the reaction product of one of the aforementioned diols or polyols and a carbonic ester and also a hydroxyl-containing (meth)acrylate.

[0078] Examples of suitable carbonic esters include ethylene carbonate, 1,2- or 1,3-propylene carbonate, dimethyl carbonate, diethyl carbonate or dibutyl carbonate.

[0079] Examples of suitable hydroxyl-containing (meth)acrylates are 2-hydroxyethyl (meth)acrylate, 2- or 3-hydroxypropyl (meth)acrylate, 1,4-butanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, glyceryl mono- and di(meth)acrylate, trimethylolpropane mono- and di(meth)acrylate, and pentaerythritol mono-, di-, and tri(meth)acrylate.

[0080] Particularly preferred carbonate (meth)acrylates are those of the formula:



in which R^{102} is H or CH_3 , X^2 is a C_2 - C_{18} alkylene group, and n_1 is an integer from 1 to 5, preferably 1 to 3.

[0081] R^{102} is preferably H and X^2 is preferably C_2 to C_{10} alkylene, examples being 1,2-ethylene, 1,2-propylene, 1,3-propylene, 1,4-butylene, and 1,6-hexylene, more preferably C_4 to C_8 alkylene. With very particular preference X^2 is C_6 alkylene.

[0082] The carbonate (meth)acrylates are preferably aliphatic carbonate (meth)acrylates.

[0083] Among the oligomers (B) urethane (meth)acrylates are particularly preferred.

[0084] A urethane (meth)acrylate may refer to a single urethane (meth)acrylate or to a mixture of different urethane (meth)acrylates. Suitable urethane (meth)acrylates can be monofunctional, but preferably are difunctional, or of higher functionality. The functionality refers to the number of (meth)acrylate functional groups exhibited by the compound.

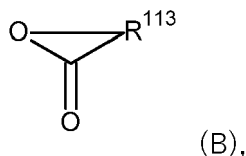
[0085] Preferred are urethane (meth)acrylates made from polyetherdiols, or polyester diols, aliphatic, aromatic, or cyclic diisocyanates and hydroxyalkyl (meth)acrylates. More preferred are urethane (meth)acrylates made from polyester diols, aromatic, or cyclic diisocyanates and hydroxyalkyl (meth)acrylates.

[0086] The diisocyanates are preferably selected from 4,4'-, 2,4'- and/or 2,2'-methylenedicyclohexyl diisocyanate

(H12MDI), isophorone diisocyanates (IPDI) and tolylene 2,4- and/or 2,6-diisocyanate (TDI).

[0087] The hydroxyalkyl (meth)acrylates are preferably selected from 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2- or 3-hydroxypropyl acrylate, 2- or 3-hydroxypropyl methacrylate, 4-hydroxybutyl methacrylate, and 4-hydroxybutyl acrylate.

[0088] Also preferred are urethane (meth)acrylates made from lactones of formula



aliphatic, aromatic, or cyclic diisocyanates and hydroxyalkyl (meth)acrylates. More preferred are urethane (meth)acrylates made from caprolactone, aliphatic, or cyclic diisocyanates and hydroxyalkyl (meth)acrylates.

[0089] The diisocyanates are preferably selected from di(isocyanatocyclohexyl)methane, 2,2,4- and 2,4,4-trimethylhexane diisocyanate, and especially 4,4'-, 2,4'- and/or 2,2'-methylenedicyclohexyl diisocyanate (H12MDI).

[0090] The hydroxyalkyl (meth)acrylates are preferably selected from 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2- or 3-hydroxypropyl acrylate, 2- or 3-hydroxypropyl methacrylate, 4-hydroxybutyl methacrylate, and 4-hydroxybutyl acrylate.

[0091] Also preferred are those having polyfunctionality of (meth)acrylates or mixed acrylic and methacrylic functionality.

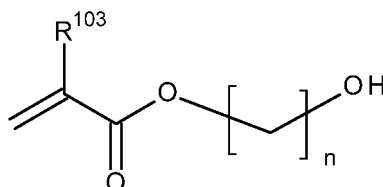
[0092] In a preferred embodiment the polyester urethane (meth)acrylate (B) is obtained by reacting

(B1) a hydroxyalkylacrylate, or hydroxyalkylmethacrylate,

(B2) an aliphatic diisocyanate, an aliphatic polyisocyanate, a cycloaliphatic diisocyanate, a cycloaliphatic polyisocyanate, an aromatic diisocyanate, or an aromatic polyisocyanate, or mixtures thereof, especially an aliphatic diisocyanate, cycloaliphatic diisocyanate, or an aromatic diisocyanate, or mixtures thereof,

(B3) a polyester polyol, which is derived from aliphatic dicarboxylic acids and aliphatic diols, and (B4) optionally a secondary polyol, especially glycerol.

[0093] The hydroxyalkylacrylate, or hydroxyalkylmethacrylate (B1) is preferably a compound of formula



wherein R^{103} is a hydrogen atom, or a methyl group, and n is 2 to 6, especially 2 to 4. Examples of (B1) include 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2- or 3-hydroxypropyl acrylate, 2- or 3-hydroxypropyl methacrylate, 4-hydroxybutyl methacrylate and 4-hydroxybutyl acrylate. 2-Hydroxyethyl acrylate is most preferred.

[0094] Hydroxyalkylacrylates, or hydroxyalkylmethacrylates (B1) having shorter alkyl chains (n is 2 to 4, especially 2) lead to a higher E modulus of the UV cured composition. Hydroxyalkylmethacrylates (B1) lead to a higher E modulus as compared to hydroxyalkylacrylates.

[0095] The organic diisocyanate (B2) used for making the polyester urethane acrylate is either an aliphatic, a cycloaliphatic, or an aromatic diisocyanate.

[0096] Examples of customary aliphatic and cycloaliphatic diisocyanates are tri-, tetra-, penta-, hexa-, hepta- and/or octamethylene diisocyanate, 2-methylpentamethylene 1,5-diisocyanate, 2-ethyltetramethylene 1,4-diisocyanate, hexamethylene 1,6-diisocyanate (HDI), pentamethylene 1,5-diisocyanate, butylene 1,4-diisocyanate, trimethylhexamethylene 1,6-diisocyanate, 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate, IPDI), 1,4- and/or 1,3-bis(isocyanatomethyl)cyclohexane (HDI), 1,4-cyclohexane diisocyanate, 1-methyl-2,4- and/or 1-methyl-2,6-cyclohexane diisocyanate, 4,4'-, 2,4'- and/or 2,2'-methylenedicyclohexyl diisocyanate (H12MDI).

[0097] Preferred aliphatic and cycloaliphatic polyisocyanates are hexamethylene 1,6-diisocyanate (HDI), 1-isocyanato-3,3,5-trimethyl-5-isocyanatomethylcyclohexane (isophorone diisocyanate, IPDI) and 4,4'-, 2,4'- and/or 2,2'-methylenedicyclohexyl diisocyanate (H12MDI); particular preference is given to H12MDI and IPDI or mixtures thereof. Suitable

aromatic diisocyanates include naphthylene 1,5- diisocyanate (NDI), tolylene 2,4- and/or 2,6-diisocyanate (TDI), diphenylmethane 2,2'-, 2,4'- and/or 4,4'-diisocyanate (MDI), 3,3'-dimethyl-4,4'-diisocyanato-diphenyl (TODI), p-phenylene diisocyanate (PDI), diphenylethane-4,4'-diisocyanate (EDI), diphenylmethane diisocyanate, 3,3'-dimethyldiphenyl-diisocyanate, 1,2-diphenylethane diisocyanate and/or phenylene diisocyanate.

[0098] The at present most preferred diisocyanates are 4,4'-, 2,4'- and/or 2,2'-methylenedicyclohexyl diisocyanate (H12MDI), isophorone diisocyanates (IPDI), or tolylene 2,4- and/or 2,6-diisocyanate (TDI).

[0099] Polyester polyols (B3) derived from dicarboxylic acid and diols are preferred and, for example, described in US20160122465. The dicarboxylic acids used for making the polyester polyol include aliphatic, or cycloaliphatic dicarboxylic acids, or combinations thereof. Among them, aliphatic dicarboxylic acids are preferred. Suitable aliphatic dicarboxylic acids which can be used alone or in mixture typically contain from 4 to 12 carbon atoms and include: succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, and the like. Adipic acid is preferred.

[0100] The diols used for making the polyester polyol include aliphatic, or cycloaliphatic diols, or combinations thereof, preferably aliphatic diols containing 2 to 8 carbon atoms and more preferably 2 to 6 carbon atoms. Some representative examples of aliphatic diols that can be used include ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol and the like.

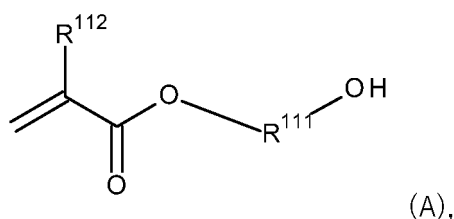
[0101] In a preferred embodiment, only one kind of aliphatic dicarboxylic acid is used in making the polyester polyol. In another preferred embodiment, one or two kinds of aliphatic diols are used in making the polyester polyol. Most preferably, the polyester polyol is derived from adipic acid and ethylene glycol and 1,4-butanediol (poly(ethylene 1,4-butylene adipate) diol, PEBA). In the PEBA, the molar ratio of ethylene glycol to 1,4-butanediol is from 0.05:1 to 10:1, preferably from 0.2:1 to 5:1, more preferably 0.5:1 to 1.5:1, most preferred from 0.75: 1 to 1.25: 1.

[0102] The linear polyester polyol will typically have a number average molecular weight within the range of 4×10^2 to 7.0×10^3 , preferably 8×10^2 to 6.0×10^3 , more preferably 1×10^3 to 5.0×10^3 . In a preferred embodiment, the linear polyol is polyester polyol derived from one kind of aliphatic dicarboxylic acid and two kinds of aliphatic diols and has a number average molecular weight of from 2.0×10^3 to 4.0×10^3 . In another preferred embodiment, the linear polyol is polyester polyol derived from one kind of aliphatic dicarboxylic acid and one kind of aliphatic diol and has a number average molecular weight of from 1.5×10^3 to 4.0×10^3 , and more preferably from 1.8×10^3 to 3.5×10^3 . All molecular weights specified in this text have the unit of [g/mol] and refer, unless indicated otherwise, to the number average molecular weight (M_n).

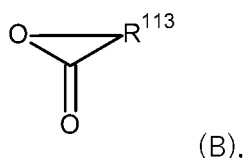
[0103] The polyester urethane acrylates, or methacrylates (A) have viscosities in the range of 2000 to 20000 mPas at 60° C.

[0104] A secondary polyol, such as, for example, glycerol, may be used, to finetune the mechanical properties of the inventive urethane (meth)acrylates by introducing linear or branched structural elements.

[0105] In another preferred embodiment the polyester urethane (meth)acrylate (B) is obtained by reacting a hydroxy-alkyl(meth)acrylate of formula



with a lactone of formula



and at least one cycloaliphatic or asymmetric aliphatic diisocyanate, wherein R^{111} is a divalent alkylene radical having 2 to 12 carbon atoms and which may optionally be substituted by C_1 - C_4 alkyl groups and/or interrupted by one or more oxygen atoms, R^{112} in each case independently of any other is methyl or hydrogen, R^{113} is a divalent alkylene radical having 1 to 12 carbon atoms and which may optionally be substituted by C_1 to C_4 alkyl groups and/or interrupted by one or more oxygen atoms. Reference is made to WO14191228A1

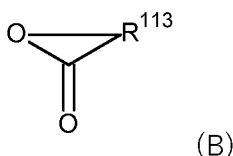
[0106] R^{111} is preferably selected from the group consisting of 1,2-ethylene, 1,2- or 1,3-propylene, 1,2-, 1,3-, or 1,4-butylene, 1,1-dimethyl-1,2-ethylene, 1,2-dimethyl-1,2-ethylene, 1,5-pentylene, 1,6-hexylene, 1,8-octylene, 1,10-de-

cylene, and 1,12-dodecylene.

[0107] R^{113} is preferably selected from the group consisting of methylene, 1,2-ethylene, 1,2-propylene, 1,3-propylene, 1,2-butylene, 1,3-butylene, 1,4-butylene, 1,5-pentylene, 1,5-hexylene, 1,6-hexylene, 1,8-octylene, 1,10-decylene, 1,12-dodecylene, 2-oxa-1,4-butylene, 3-oxa-1,5-pentylene, and 3-oxa-1,5-hexylene.

[0108] The hydroxyalkyl(meth)acrylate of formula (A) is preferably selected from the group consisting of 2-hydroxyethyl(meth)acrylate, 2- or 3-hydroxypropyl(meth)acrylate, 1,4-butanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, 1,5-pentanediol mono(meth)acrylate, and 1,6-hexanediol mono(meth)acrylate.

[0109] The lactone of formula



is preferably selected from the group consisting of β -propiolactone, γ -butyrolactone, γ -ethyl-gamma-butyrolactone, γ -valerolactone, delta-valerolactone, ϵ -caprolactone, 7-methyloxepan-2-one, 1,4-dioxepan-5-one, oxacyclotridecan-2-one, and 13-butyl-oxacyclotridecan-2-one.

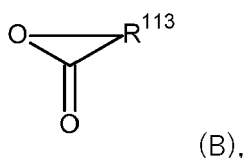
[0110] Cycloaliphatic diisocyanates are 1,4-, 1,3-, or 1,2-diisocyanatocyclohexane, 4,4'-, 2,4'- and/or 2,2'-methylenedicyclohexyl diisocyanate (H12MDI), bis(isocyanatomethyl)bicyclo[2.2.1]heptane (NBDI), 1-isocyanato-3,3,5-trimethyl-5-(isocyanatomethyl)cyclohexane(isophorone diisocyanate), 1,3- or 1,4-bis(isocyanatomethyl)cyclohexane or 2,4- or 2,6-diisocyanato-1-methylcyclohexane, and also 3(or 4),8(or 9)-bis(isocyanatomethyl)tricyclo[5.2.1.0^{2,6}]decane isomer mixtures.

[0111] Asymmetric aliphatic diisocyanates are derivatives of lysine diisocyanate, or tetramethylxylene diisocyanate, trimethylhexane diisocyanate, or tetramethylhexane diisocyanate.

[0112] Very particular preference is given to di(isocyanatocyclohexyl)methane, 2,2,4- and 2,4,4-trimethylhexane diisocyanate, and especially 4,4'-, 2,4'- and/or 2,2'-methylenedicyclohexyl diisocyanate (H12MDI).

[0113] The urethane (meth)acrylates can be in particular produced by reacting ϵ -caprolactone, 4,4'-, 2,4'- and/or 2,2'-methylenedicyclohexyl diisocyanate (H12MDI) and hydroxyethylacrylate.

[0114] In another preferred embodiment the polyester urethane (meth)acrylate (B) is obtained by reacting a polyalkylene glycol with a lactone of formula



at least one cycloaliphatic or asymmetric aliphatic diisocyanate, and an hydroxyalkyl(meth)acrylate of formula (A).

[0115] The hydroxyalkyl(meth)acrylate of formula (A) is preferably selected from the group consisting of 2-hydroxyethyl(meth)acrylate, 2- or 3-hydroxypropyl(meth)acrylate, 1,4-butanediol mono(meth)acrylate, neopentyl glycol mono(meth)acrylate, 1,5-pentanediol mono(meth)acrylate, and 1,6-hexanediol mono(meth)acrylate.

[0116] The urethane (meth)acrylates can be in particular produced by reacting a polyalkylene glycol, preferably a polyethylene glycol, with ϵ -caprolactone, 4,4'-, 2,4'- and/or 2,2'-methylenedicyclohexyl diisocyanate (H12MDI) and hydroxyethylacrylate.

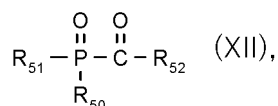
Photoinitiator (C)

[0117] The photoinitiator (C) may be a single compound, or a mixture of compounds.

[0118] Examples of photoinitiators (C) are known to the person skilled in the art and for example published by Kurt Dietliker in "A compilation of photoinitiators commercially available for UV today", Sita Technology Textbook, Edinburgh, London, 2002.

[0119] In a preferred embodiment the photoinitiator (C) is selected from acylphosphine oxide compounds, benzophenone compounds, alpha-aminoketone compounds, phenylglyoxylate compounds, oxime ester compounds, mixtures thereof and mixtures with alpha-hydroxy ketone compounds, or alpha-alkoxyketone compounds.

[0120] Examples of suitable acylphosphine oxide compounds are of the formula XII



wherein

R_{50} is unsubstituted cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenyl; or is cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenyl substituted by one or more halogen, $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_1\text{-C}_{12}$ alkylthio or by $\text{NR}_{53}\text{R}_{54}$; or R_{50} is unsubstituted $\text{C}_1\text{-C}_{20}$ alkyl or is $\text{C}_1\text{-C}_{20}$ alkyl which is substituted by one or more halogen, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_1\text{-C}_{12}$ alkylthio, $\text{NR}_{53}\text{R}_{54}$ or by $-(\text{CO})\text{-O-C}_1\text{-C}_{24}$ alkyl;

R_{51} is unsubstituted cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenyl; or is cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenyl substituted by one or more halogen, $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_1\text{-C}_{12}$ alkylthio or by $\text{NR}_{53}\text{R}_{54}$; or R_{51} is $-(\text{CO})\text{R}'_{52}$; or R_{51} is $\text{C}_1\text{-C}_{12}$ alkyl which is unsubstituted or substituted by one or more halogen, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_1\text{-C}_{12}$ alkylthio, or by $\text{NR}_{53}\text{R}_{54}$;

R_{52} and R'_{52} independently of each other are unsubstituted cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenyl, or are cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenyl substituted by one or more halogen, $\text{C}_1\text{-C}_4$ alkyl or $\text{C}_1\text{-C}_4$ alkoxy; or R_{52} is a 5- or 6-membered heterocyclic ring comprising an S atom or N atom;

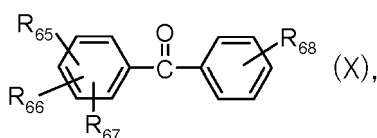
R_{53} and R_{54} independently of one another are hydrogen, unsubstituted $\text{C}_1\text{-C}_{12}$ alkyl or $\text{C}_1\text{-C}_{12}$ alkyl substituted by one or more OH or SH wherein the alkyl chain optionally is interrupted by one to four oxygen atoms; or R_{53} and R_{54} independently of one another are $\text{C}_2\text{-C}_{12}$ -alkenyl, cyclopentyl, cyclohexyl, benzyl or phenyl;

[0121] In a particularly preferred embodiment the photoinitiator (C) is a compound of the formula (XII), such as, for example, bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide; 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide; ethyl (2,4,6-trimethylbenzoyl phenyl) phosphinic acid ester; (2,4,6-trimethylbenzoyl)-2,4-dipentoxyphenylphosphine oxide and bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide.

[0122] Interesting further are mixtures of the compounds of the formula (XII) with compounds of the formula (XI) as well as mixtures of different compounds of the formula (XII).

[0123] Examples are mixtures of bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide with 1-hydroxy-cyclohexyl-phenyl-ketone, of bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide with 2-hydroxy-2-methyl-1-phenyl-propan-1-one, of bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide with ethyl (2,4,6-trimethylbenzoyl phenyl) phosphinic acid ester, etc.

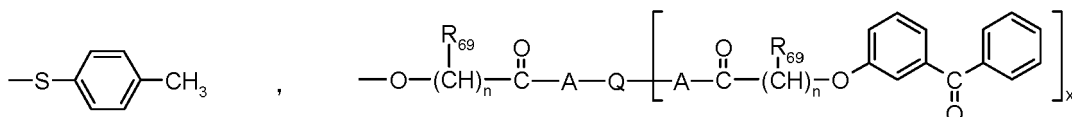
[0124] Examples of suitable benzophenone compounds are compounds of the formula



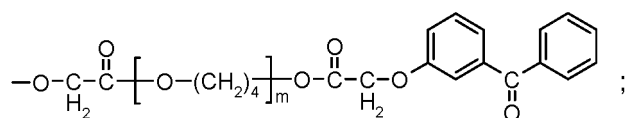
wherein

R_{65} , R_{66} and R_{67} independently of one another are hydrogen, $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ -halogenalkyl, $\text{C}_1\text{-C}_4$ alkoxy, Cl or $\text{N}(\text{C}_1\text{-C}_4\text{alkyl})_2$;

R_{68} is hydrogen, $\text{C}_1\text{-C}_4$ alkyl, $\text{C}_1\text{-C}_4$ halogenalkyl, phenyl, $\text{N}(\text{C}_1\text{-C}_4\text{alkyl})_2$, COOCH_3 ,



or



x is a number greater than 1 but no greater than the number of available hydroxyl groups in Q;

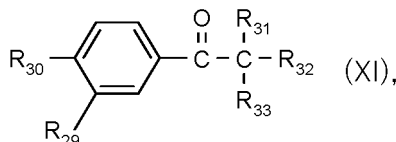
R_{69} and $R_{69'}$, independently of one another are hydrogen, methyl or ethyl; and if n (or a) is greater than 1 the radicals

a is a number from 1 to 2;

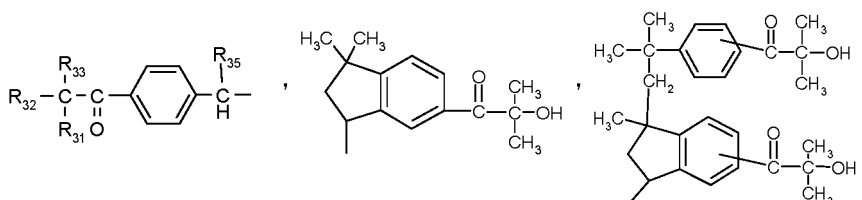
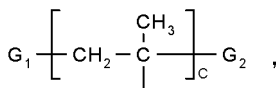
y is a number from 1 to 10:

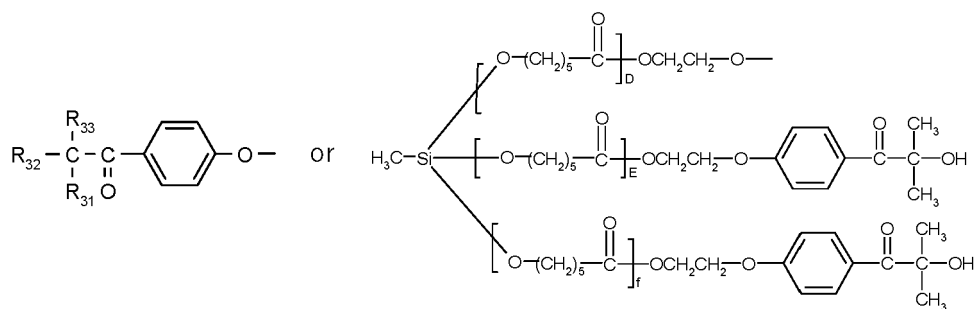
m is an integer 2-10.

[0126] Examples of suitable alpha-hydroxy ketone, alpha-alkoxyketone or alpha-aminoketone compounds are of the formula



R₂₉ is hydrogen or C₁-C₁₈alkoxy;



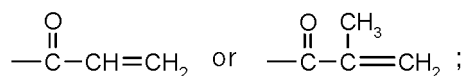


D, E and f are 1-3;

c is 2-10;

G₁ and G₂ independently of one another are end groups of the polymeric structure, preferably hydrogen or methyl;

R₃₄ is hydrogen,



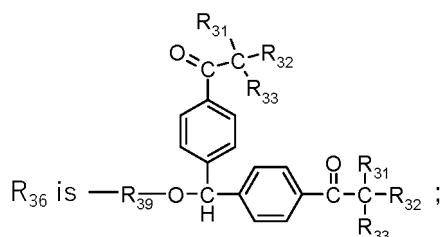
R₃₁ is hydroxy, C₁-C₁₆alkoxy, morpholino, dimethylamino or -O(CH₂CH₂O)_g-C₁-C₁₆alkyl;

g is 1-20;

R₃₂ and R₃₃ independently of one another are hydrogen, C₁-C₆alkyl, C₁-C₁₆alkoxy or -O(CH₂CH₂O)_g-C₁-C₁₆alkyl; or are unsubstituted phenyl or benzyl; or phenyl or benzyl substituted by C₁-C₁₂alkyl; or R₃₂ and R₃₃ together with the carbon atom to which they are attached form a cyclohexyl ring;

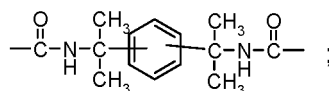
R₃₅ is hydrogen, OR₃₆ or NR₃₇R₃₈;

R₃₆ is hydrogen, C₁-C₁₂alkyl which optionally is interrupted by one or more non-consecutive O-atoms and which uninterrupted or interrupted C₁-C₁₂alkyl optionally is substituted by one or more OH, or



R₃₇ and R₃₈ independently of each other are hydrogen or C₁-C₁₂alkyl which is unsubstituted or is substituted by one or more OH;

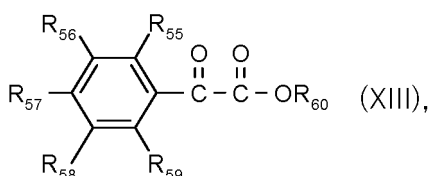
R₃₉ is C₁-C₁₂alkylene which optionally is interrupted by one or more non-consecutive O, - (CO)-NH-C₁-C₁₂alkylene-NH-(CO)- or



with the proviso that R₃₁, R₃₂ and R₃₃ not all together are C₁-C₁₆alkoxy or -O(CH₂CH₂O)_g-C₁-C₁₆alkyl.

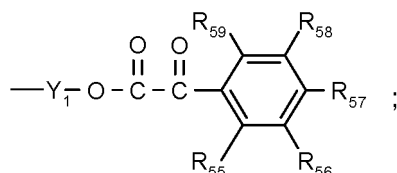
[0127] Specific examples are 1-hydroxy-cyclohexyl-phenyl-ketone or a mixture of 1-hydroxy-cyclohexyl-phenyl-ketone with benzophenone), 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropan-1-one, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butan-1-one, 2-dimethylamino-2-(4-methyl-benzyl)-1-(4-morpholin-4-yl-phenyl)-butan-1-one, (3,4-dimethoxy-benzoyl)-1-benzyl-1-dimethylamino propane, 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propan-1-one, 2,2-dimethoxy-1,2-diphenylethan-1-one, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, 2-hydroxy-1-[4-[4-(2-hydroxy-2-methylpropionyl)-benzyl]-phenyl]-2-methyl-propan-1-one, 2-hydroxy-1-[4-[4-(2-hydroxy-2-methyl-propionyl)-phenoxy]-phenyl]-2-methyl-propan-1-one, Esacure KIP provided by IGM, 2-hydroxy-1-[1-[4-(2-hydroxy-2-methyl-propionyl)-phenyl]-1,3,3-trimethyl-indan-5-yl]-2-methyl-propan-1-one.

[0128] Examples of suitable phenylglyoxylate compounds are of the formula



wherein

R_{60} is hydrogen, $\text{C}_1\text{-C}_{12}$ alkyl or



R_{55} , R_{56} , R_{57} , R_{58} and R_{59} independently of one another are hydrogen, unsubstituted $\text{C}_1\text{-C}_{12}$ alkyl or $\text{C}_1\text{-C}_{12}$ alkyl substituted by one or more OH, $\text{C}_1\text{-C}_4$ alkoxy, phenyl, naphthyl, halogen or by CN; wherein the alkyl chain optionally is interrupted by one or more oxygen atoms; or

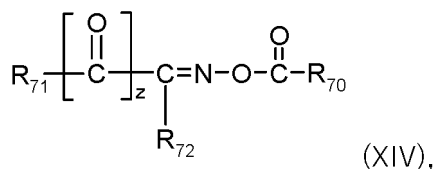
R_{55} , R_{56} , R_{57} , R_{58} and R_{59} independently of one another are $\text{C}_1\text{-C}_4$ alkoxy, $\text{C}_1\text{-C}_4$ alkylthio or $\text{NR}_{52}\text{R}_{53}$;

R_{52} and R_{53} independently of one another are hydrogen, unsubstituted $\text{C}_1\text{-C}_{12}$ alkyl or $\text{C}_1\text{-C}_{12}$ alkyl substituted by one or more OH or SH wherein the alkyl chain optionally is interrupted by one to four oxygen atoms; or R_{52} and R_{53} independently of one another are $\text{C}_2\text{-C}_{12}$ -alkenyl, cyclopentyl, cyclohexyl, benzyl or phenyl; and

Y_1 is $\text{C}_1\text{-C}_{12}$ alkylene optionally interrupted by one or more oxygen atoms.

[0129] Specific examples of the compounds of the formula XIII are oxo-phenyl-acetic acid 2-[2-(2-oxo-2-phenyl-acetoxy)-ethoxy]-ethyl ester (Irgacure[®]754), methyl α -oxo benzeneacetate.

[0130] Examples of suitable oxime ester compounds are of the formula

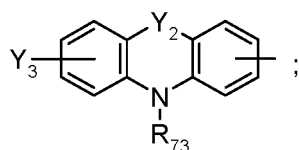


wherein z is 0 or 1;

R_{70} is hydrogen, $\text{C}_3\text{-C}_8$ cycloalkyl; $\text{C}_1\text{-C}_{12}$ alkyl which is unsubstituted or substituted by one or more halogen, phenyl or by CN; or R_{70} is $\text{C}_2\text{-C}_5$ alkenyl; phenyl which is unsubstituted or substituted by one or more $\text{C}_1\text{-C}_6$ alkyl, halogen, CN, OR_{73} , SR_{74} or by $\text{NR}_{75}\text{R}_{76}$; or R_{70} is $\text{C}_1\text{-C}_8$ alkoxy, benzyloxy; or phenoxy which is unsubstituted or substituted by one or more $\text{C}_1\text{-C}_6$ alkyl or by halogen;

R_{71} is phenyl, naphthyl, benzoyl or naphthoyl, each of which is substituted by one or more halogen, $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_3\text{-C}_8$ cycloalkyl, benzyl, phenoxycarbonyl, $\text{C}_2\text{-C}_{12}$ alkoxycarbonyl, OR_{73} , SR_{74} , SOR_{74} , SO_2R_{74} or by $\text{NR}_{75}\text{R}_{76}$, wherein the substituents OR_{73} , SR_{74} and $\text{NR}_{75}\text{R}_{76}$ optionally form 5- or 6-membered rings *via* the radicals R_{73} , R_{74} , R_{75} and/or R_{76} with further substituents on the phenyl or naphthyl ring; or each of which is substituted by phenyl or by phenyl which is substituted by one or more OR_{73} , SR_{74} or by $\text{NR}_{75}\text{R}_{66}$;

or R_{71} is thioxanthyl, or



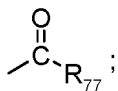
R_{72} is hydrogen; unsubstituted $\text{C}_1\text{-C}_{20}$ alkyl or $\text{C}_1\text{-C}_{20}$ alkyl which is substituted by one or more halogen, OR_{73} , SR_{74} ,

C₃-C₈cycloalkyl or by phenyl; or is C₃-C₈cycloalkyl; or is phenyl which is unsubstituted or substituted by one or more C₁-C₆alkyl, phenyl, halogen, OR₇₃, SR₇₄ or by NR₇₅R₇₆; or is C₂-C₂₀alkanoyl or benzoyl which is unsubstituted or substituted by one or more C₁-C₆alkyl, phenyl, OR₇₃, SR₇₄ or by NR₇₅R₇₆; or is C₂-C₁₂alkoxycarbonyl, phenoxy-carbonyl, CN, CONR₇₅R₇₆, NO₂, C₁-C₄haloalkyl, S(O)_y-C₁-C₆alkyl, or S(O)_y-phenyl,

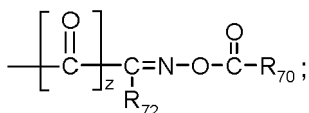
y is 1 or 2;

Y₂ is a direct bond or no bond;

Y₃ is NO₂ or



R₇₃ and R₇₄ independently of one another are hydrogen, C₁-C₂₀alkyl, C₂-C₁₂alkenyl, C₃-C₈cycloalkyl, C₃-C₈cycloalkyl which is interrupted by one or more, preferably 2, O, phenyl-C₁-C₃alkyl; or are C₁-C₈alkyl which is substituted by OH, SH, CN, C₁-C₈alkoxy, C₁-C₈alkanoyl, C₃-C₈cycloalkyl, by C₃-C₈cycloalkyl which is interrupted by one or more O, or which C₁-C₈alkyl is substituted by benzoyl which is unsubstituted or substituted by one or more C₁-C₆alkyl, halogen, OH, C₁-C₄alkoxy or by C₁-C₄alkylsulfanyl; or are phenyl or naphthyl, each of which is unsubstituted or substituted by halogen, C₁-C₁₂alkyl, C₁-C₁₂alkoxy, phenyl-C₁-C₃alkoxy, phenoxy, C₁-C₁₂alkylsulfanyl, phenylsulfanyl, N(C₁-C₁₂alkyl)₂, diphenylamino or by



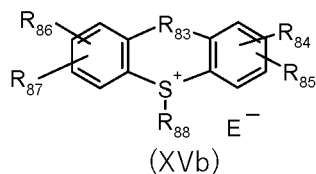
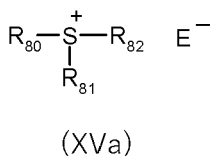
R₇₅ and R₇₆ independently of each other are hydrogen, C₁-C₂₀alkyl, C₂-C₄hydroxyalkyl, C₂-C₁₀alkoxyalkyl, C₂-C₅alkenyl, C₃-C₈cycloalkyl, phenyl-C₁-C₃alkyl, C₁-C₈alkanoyl, C₃-C₁₂alkenoyl, benzoyl; or are phenyl or naphthyl, each of which is unsubstituted or substituted by C₁-C₁₂alkyl, benzoyl or by C₁-C₁₂alkoxy; or R₇₅ and R₇₆ together are C₂-C₆alkylene optionally interrupted by O or NR₇₃ and optionally are substituted by hydroxyl, C₁-C₄alkoxy, C₂-C₄alkanoyloxy or by benzoyloxy;

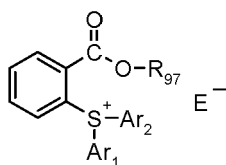
R₇₇ is C₁-C₁₂alkyl, thienyl or phenyl which is unsubstituted or substituted by C₁-C₁₂alkyl, OR₇₃, morpholino or by N-carbazolyl.

[0131] Specific examples are 1,2-octanedione 1-[4-(phenylthio)phenyl]-2-(O-benzoyloxime), ethanone 1-[9-ethyl-6-(2-methylbenzoyl)-9H-carbazol-3-yl]-1-(O-acetyloxime), 9H-thioxanthene-2-carboxaldehyde 9-oxo-2-(O-acetyloxime), ethanone 1-[9-ethyl-6-(4morpholinobenzoyl)-9H-carbazol-3-yl]-1-(O-acetyloxime), ethanone 1-[9-ethyl-6-(2-methyl-4-(2-(1,3-dioxo-2-dimethyl-cyclopent-5-yl)ethoxy)-benzoyl)-9H-carbazol-3-yl]-1-(O-acetyloxime) (Adeka N-1919), ethanone 1-[9-ethyl-6-nitro-9H-carbazol-3-yl]-1-[2-methyl-4-(1-methyl-2-methoxy)ethoxy]phenyl]-1-(O-acetyloxime) (Adeka NCI831), etc.

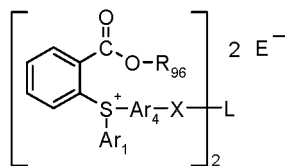
[0132] It is also possible to add cationic photoinitiators, such as benzoyl peroxide (other suitable peroxides are described in US 4 950 581, column 19, lines 17-25), or aromatic sulfonium, phosphonium or iodonium salts, such as are described, for example, in US 4 950 581, column 18, line 60 to column 19, line 10.

[0133] Suitable sulfonium salt compounds are of formula

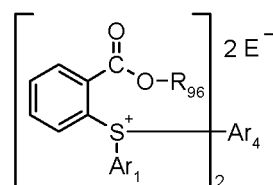




(XVc)



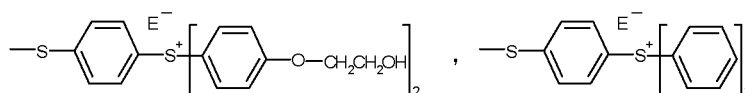
(XVd)



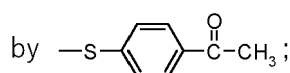
(XVe)

wherein

R₈₀, R₈₁ and R₈₂ are each independently of the others unsubstituted phenyl, or phenyl substituted by -S-phenyl,



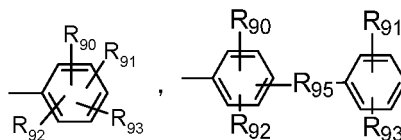
or



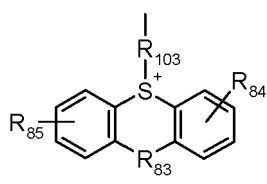
R₈₃ is a direct bond, S, O, CH₂, (CH₂)₂, CO or NR₈₉;

R₈₄, R₈₅, R₈₆ and R₈₇ independently of one another are hydrogen, C₁-C₂₀alkyl, C₃-C₈cycloalkyl, C₁-C₂₀alkoxy, C₂-C₂₀alkenyl, CN, OH, halogen, C₁-C₆alkylthio, phenyl, naphthyl, phenyl-C₁-C₇alkyl, naphthyl-C₁-C₃alkyl, phenoxy, naphthoxy, phenyl-C₁-C₇alkyloxy, naphthyl-C₁-C₃alkyloxy, phenyl-C₂-C₆alkenyl, naphthyl-C₂-C₄alkenyl, S-phenyl, (CO)R₈₉, O(CO)R₈₉, (CO)OR₈₉, SO₂R₈₉ or OSO₂R₈₉;

R₈₈ is C₁-C₂₀alkyl, C₁-C₂₀hydroxyalkyl,



or



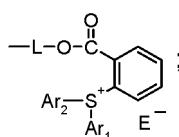
R₈₉ is hydrogen, C₁-C₁₂alkyl, C₁-C₁₂hydroxyalkyl, phenyl, naphthyl or biphenyl;

R₉₀, R₉₁, R₉₂ and R₉₃ independently of one another have one of the meanings as given for R₈₄; or R₉₀ and R₉₁ are joined to form a fused ring system with the benzene rings to which they are attached;

R₉₅ is a direct bond, S, O or CH₂;

R₉₆ is hydrogen, C₁-C₂₀alkyl; C₂-C₂₀alkyl interrupted by one or more O; or is -L-M-R₉₈ or -L-R₉₈;

R₉₇ has one of the meanings as given for R₉₆ or is



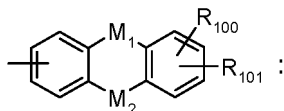
R_{98} is a monovalent sensitizer or photoinitiator moiety;

Ar_7 and Ar_2 independently of one another are phenyl unsubstituted or substituted by C_1 - C_{20} alkyl, halogen or OR_{99} ;

or are unsubstituted naphthyl, anthryl, phenanthryl or biphenyl;

or are naphthyl, anthryl, phenanthryl or biphenyl substituted by C_1 - C_{20} alkyl, OH or OR_{99} ;

or are $-Ar_4-A_1-Ar_3$ or



Ar_3 is unsubstituted phenyl, naphthyl, anthryl, phenanthryl or biphenyl;

or is phenyl, naphthyl, anthryl, phenanthryl or biphenyl substituted by C_1 - C_{20} alkyl, OR_{99} or benzoyl;

Ar_4 is phenylene, naphthylene, anthrylene or phenanthrylene;

A_1 is a direct bond, S, O or C_1 - C_{20} alkylene;

X is CO, C(O)O, OC(O), O, S or NR_{99} ;

L is a direct bond, S, O, C_1 - C_{20} alkylene or C_2 - C_{20} alkylene interrupted by one or more non-consecutive O;

R_{99} is C_1 - C_{20} alkyl or C_1 - C_{20} hydroxyalkyl; or is C_1 - C_{20} alkyl substituted by $O(CO)R_{102}$;

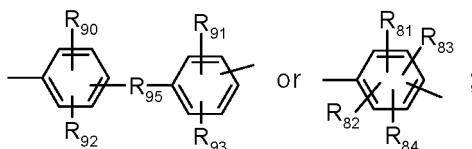
M_1 is S, CO or NR_{100} ;

M_2 is a direct bond, CH_2 , O or S;

R_{100} and R_{101} independently of one another are hydrogen, halogen, C_1 - C_8 alkyl, C_1 - C_8 alkoxy or phenyl;

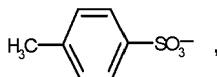
R_{102} is C_1 - C_{20} alkyl;

R_{103} is

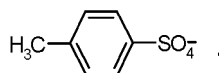


and

E is an anion, especially PF_6^- , SbF_6^- , AsF_6^- , BF_4^- , $(C_6F_5)_4B^-$, Cl, Br, HSO_4^- , $CF_3-SO_3^-$, $F-SO_3^-$,

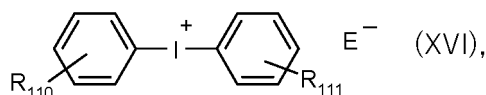


$CH_3-SO_3^-$, ClO_4^- , PO_4^{3-} , NO_3^- , SO_4^{2-} , $CH_3-SO_4^-$, or



[0134] Specific examples of sulfonium salt compounds are for example Irgacure[®]270 (BASF SE); Cyacure[®] UVI-6990, Cyacure[®]UVI-6974 (Union Carbide), Degacure[®]KI 85 (Degussa), SP-55, SP-150, SP-170 (Asahi Denka), GE UVE 1014 (General Electric), SarCat[®] KI-85 (= triarylsulfonium hexafluorophosphate; Sartomer), SarCat[®] CD 1010 (= mixed triarylsulfonium hexafluoroantimonate; Sartomer); SarCat[®] CD 1011 (= mixed triarylsulfonium hexafluorophosphate; Sartomer),

[0135] Suitable iodonium salt compounds are of formula

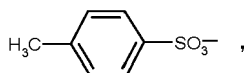


wherein

R_{110} and R_{111} are each independently of the other hydrogen, C_1 - C_{20} alkyl, C_1 - C_{20} alkoxy, OH-substituted

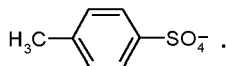
C₁-C₂₀alkoxy, halogen, C₂-C₁₂alkenyl, C₃-C₈cycloalkyl, especially methyl, isopropyl or isobutyl; and E is an anion, especially PF₆, SbF₆, AsF₆, BF₄, (C₆F₅)₄B, Cl, Br, HSO₄, CF₃-SO₃, F-SO₃,

5



CH₃-SO₃, ClO₄, PO₄, NO₃, SO₄, CH₃-SO₄ or

10



[0136] Specific examples of iodonium salt compounds are e.g. tolylcumyliodonium tetrakis(pentafluorophenyl) borate, 4-[(2-hydroxy-tetradecyloxy)phenyl]phenyliodonium hexafluoroantimonate or hexafluorophosphate, tolylcumyliodonium hexafluorophosphate, 4-isopropylphenyl-4'-methylphenyliodonium hexafluorophosphate, 4-isobutylphenyl-4'-methylphenyliodonium hexafluorophosphate (Irgacure® 250, BASF SE), 4-octyloxyphenyl-phenyliodonium hexafluorophosphate or hexafluoroantimonate, bis(dodecylphenyl)iodonium hexafluoroantimonate or hexafluorophosphate, bis(4-methylphenyl)iodonium hexafluorophosphate, bis(4-methoxyphenyl)iodonium hexafluorophosphate, 4-methylphenyl-4'-ethoxyphenyliodonium hexafluorophosphate, 4-methylphenyl-4'-dodecyl-phenyliodonium hexafluorophosphate, 4-methylphenyl-4'-phenoxyphenyliodonium hexafluorophosphate.

[0137] Of all the iodonium salts mentioned, compounds with other anions are, of course, also suitable. The preparation of iodonium salts is known to the person skilled in the art and described in the literature, for example US 4151175, US 3862333, US 4694029, EP 562897, US 4399071, US 6306555, WO 98/46647 J. V. Crivello, "Photoinitiated Cationic Polymerization" in: UV Curing: Science and Technology, Editor S. P. Pappas, pages 24-77, Technology Marketing Corporation, Norwalk, Conn. 1980, ISBN No. 0-686-23773-0; J. V. Crivello, J. H. W. Lam, Macromolecules, 10, 1307 (1977) and J. V. Crivello, Ann. Rev. Mater. Sci. 1983, 13, pages 173-190 and J. V. Crivello, Journal of Polymer Science, Part A: Polymer Chemistry, Vol. 37, 4241-4254 (1999).

[0138] Acylphosphinoxides, such as, for example, bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide and ethyl phenyl(2,4,6-trimethylbenzoyl)phosphinate, are preferred for curing with light sources having emission peak(s) in the UV-A range and (near) VIS range (Laser, LEDs, LCD). alpha-Hydroxy ketone type compounds, such as, for example, 1-hydroxy-cyclohexyl-phenyl-ketone, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-benzyl]-phenyl}-2-methyl-propan-1-one, 1-[4-(2-hydroxyethoxy)-phenyl]-2-hydroxy-2-methyl-1-propan-1-one, Esacure KIP provided by Lamberti, 2-hydroxy-1-{1-[4-(2-hydroxy-2-methyl-propionyl)-phenyl]-1,3,3-trimethyl-indan-5-yl}-2-methyl-propan-1-one and mixtures thereof, are preferred for curing with UV laser having emission peak at 355 nm (SLA).

[0139] If the light source emits radiation over a broad range, UV and visible range (e.g. mercury bilbs), or light sources of different wavelengths are combined (e.g. LEDs, laser), the absorption range of one photoinitiator might not cover the entire range. This can be achieved by combining two different photoinitiator types, e.g. alpha-hydroxy ketones (1-hydroxy-cyclohexyl-phenyl-ketone, 2-hydroxy-2-methyl-1-phenyl-propan-1-one, or 2-hydroxy-1-{4-[4-(2-hydroxy-2-methyl-propionyl)-benzyl]-phenyl}-2-methyl-propan-1-one) with acyl phosphinoxides (bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide, 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide and ethyl phenyl(2,4,6-trimethylbenzoyl)phosphinate. If visible radiation is used for curing specific photoinitiators like titanocenes, such as, for example, bis(cyclopentadienyl) bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium (Omnirad 784) are required.

[0140] The photoinitiators are used typically in a proportion of from about 0.5 to 10 % by weight, especially 0.1 to 5.0% by weight based on the total weight of composition.

[0141] Halogen is fluorine, chlorine, bromine and iodine.

[0142] C₁-C₂₄alkyl (C₁-C₂₀alkyl, especially C₁-C₁₂alkyl) is typically linear or branched, where possible. Examples are methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethylpropyl, 1,1,3,3-tetramethylpentyl, n-hexyl, 1-methylhexyl, 1,1,3,3,5,5-hexamethylhexyl, n-heptyl, isoheptyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 1,1,3,3-tetramethylbutyl and 2-ethylhexyl, n-nonyl, decyl, undecyl, dodecyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, or octadecyl. C₁-C₈alkyl is typically methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl, n-pentyl, 2-pentyl, 3-pentyl, 2,2-dimethyl-propyl, n-hexyl, n-heptyl, n-octyl, 1,1,3,3-tetramethylbutyl and 2-ethylhexyl. C₁-C₄alkyl is typically methyl, ethyl, n-propyl, isopropyl, n-butyl, sec.-butyl, isobutyl, tert.-butyl.

[0143] C₂-C₁₂alkenyl (C₂-C₅alkenyl) groups are straight-chain or branched alkenyl groups, such as e.g. vinyl, allyl, methallyl, isopropenyl, 2-butenyl, 3-butenyl, isobutenyl, n-penta-2,4-dienyl, 3-methyl-but-2-enyl, n-oct-2-enyl, or n-dodec-2-enyl.

[0144] C₁-C₁₂alkoxy groups (C₁-C₈alkoxy groups) are straight-chain or branched alkoxy groups, e.g. methoxy, ethoxy, n-propoxy, isopropoxy, n-butoxy, sec-butoxy, tert-butoxy, amyloxy, isoamyloxy or tert-amyloxy, heptyloxy, octyloxy, isooctyloxy, nonyloxy, decyloxy, undecyloxy and dodecyloxy.

[0145] C₁-C₁₂alkylthio groups (C₁-C₈ alkylthio groups) are straight-chain or branched alkylthio groups and have the same preferences as the alkoxy groups, except that oxygen is exchanged against sulfur.

[0146] C₁-C₁₂alkylene is bivalent C₁-C₁₂alkyl, i.e. alkyl having two (instead of one) free valencies, e.g. trimethylene or tetramethylene.

[0147] A cycloalkyl group is typically C₃-C₈cycloalkyl, such as, for example, cyclopentyl, cyclohexyl, cycloheptyl, or cyclooctyl, which may be unsubstituted or substituted.

[0148] In several cases it is advantageous to in addition to the photoinitiator employ a sensitizer compound. Examples of suitable sensitizer compounds are disclosed in WO 06/008251, page 36, line 30 to page 38, line 8.

[0149] As sensitizer inter alia benzophenone compounds as described above can be employed.

[0150] If desired, the photocurable compositions may comprise further mixture constituents which are preferably selected from

- at least one component D which is in turn selected from
 - (D.4) defoamers and deaerating agents;
 - (D.5) lubricants and leveling agents;
 - (D.6) thermally curing and/or radiation-curing auxiliaries;
 - (D.7) substrate wetting auxiliaries;
 - (D.8) wetting and dispersing auxiliaries;
 - (D.9) hydrophobizing agents;
 - (D.10) in-can stabilizers; and
 - (D.11) auxiliaries for improving scratch resistance;

- at least one component E which is in turn selected from
 - (E.1) dyes; and
 - (E.2) pigments;

- at least one component F which is in turn selected from light, heat and oxidation stabilizers; and

- at least one component G which is in turn selected from IR-absorbing compounds.

[0151] The effect of the defoamers and deaerating agents (D.4), lubricants and leveling agents (D.5), thermally curing or radiation-curing auxiliaries (D.6), substrate wetting auxiliaries (D.7), wetting and dispersing auxiliaries (D.8), hydrophobizing agents (D.9), in-can stabilizers (D.10) and auxiliaries for improving scratch resistance (D.11) listed under component D usually cannot be strictly distinguished from one another. For instance, lubricants and leveling agents often additionally act as defoamers and/or deaerating agents and/or as auxiliaries for improving scratch resistance. Radiation-curing auxiliaries can in turn act as lubricants and leveling agents and/or deaerating agents and/or also as substrate wetting auxiliaries. In accordance with the above statements, a certain additive may therefore be attributed to more than one of the groups (D.4) to (D.11) described below.

[0152] The defoamers of group (D.4) include silicon-free and silicon-containing polymers. The silicon-containing polymers are, for example, unmodified or modified polydialkylsiloxanes or branched copolymers, comb copolymers or block copolymers composed of polydialkylsiloxane and polyether units, the latter being obtainable from ethylene oxide or propylene oxide.

[0153] The deaerating agents of group (D.4) include, for example, organic polymers, for instance polyethers and polyacrylates, dialkylpolysiloxanes, especially dimethylpolysiloxanes, organically modified polysiloxanes, for instance arylalkyl-modified polysiloxanes, or else fluorosilicones. The action of defoamers is based essentially on preventing foam formation or destroying foam which has already formed. Deaerating agents act essentially in such a way that they promote the coalescence of finely distributed gas or air bubbles to larger bubbles in the medium to be deaerated, for example the inventive compositions, and hence accelerate the escape of the gas (or of the air). Since defoamers can often also be used as deaerating agents and vice versa, these additives have been combined together under group (D.4). Such auxiliaries are, for example, obtainable commercially from Tego as TEGO® Foamex 800, TEGO® Foamex 805, TEGO® Foamex 810, TEGO® Foamex 815, TEGO® Foamex 825, TEGO® Foamex 835, TEGO® Foamex 840, TEGO® Foamex 842, TEGO® Foamex 1435, TEGO® Foamex 1488, TEGO® Foamex 1495, TEGO® Foamex 3062, TEGO® Foamex 7447, TEGO® Foamex 8020, Tego® Foamex N, TEGO® Foamex K 3, TEGO® Antifoam 2-18, TEGO® Antifoam 2-57, TEGO® Antifoam 2-80, TEGO® Antifoam 2-82, TEGO® Antifoam 2-89, TEGO® Antifoam 2-92, TEGO® Antifoam 14, TEGO® Antifoam 28, TEGO® Antifoam 81, TEGO® Antifoam D 90, TEGO® Antifoam 93, TEGO® Antifoam 200, TEGO® Antifoam 201, TEGO® Antifoam 202, TEGO® Antifoam 793, TEGO® Antifoam 1488, TEGO® Antifoam 3062, TEGOPREN® 5803, TEGOPREN® 5852, TEGOPREN® 5863, TEGOPREN® 7008, TEGO® Antifoam 1-60, TEGO®

Antifoam 1-62, TEGO® Antifoam 1-85, TEGO® Antifoam 2-67, TEGO® Antifoam WM 20, TEGO® Antifoam 50, TEGO® Antifoam 105, TEGO® Antifoam 730, TEGO® Antifoam MR 1015, TEGO® Antifoam MR 1016, TEGO® Antifoam 1435, TEGO® Antifoam N, TEGO® Antifoam KS 6, TEGO® Antifoam KS 10, TEGO® Antifoam KS 53, TEGO® Antifoam KS 95, TEGO® Antifoam KS 100, TEGO® Antifoam KE 600, TEGO® Antifoam KS 911, TEGO® Antifoam MR 1000, TEGO® Antifoam KS 1100, Tego® Airex 900, Tego® Airex 910, Tego® Airex 931, Tego® Airex 935, Tego® Airex 960, Tego® Airex 970, Tego® Airex 980 and Tego® Airex 985, and from BYK as BYK®-011, BYK®-019, BYK®-020, BYK®-021, BYK®-022, BYK®-023, BYK®-024, BYK®-025, BYK®-027, BYK®-031, BYK®-032, BYK®-033, BYK®-034, BYK®-035, BYK®-036, BYK®-037, BYK®-045, BYK®-051, BYK®-052, BYK®-053, BYK®-055, BYK®-057, BYK®-065, BYK®-067, BYK®-070, BYK®-080, BYK®-088, BYK®-141 and BYK®-A 530.

[0154] The auxiliaries of group (D.4) are typically used in a proportion of from about 0.05 to 3.0% by weight, preferably from about 0.5 to 2.0% by weight, based on the total weight of the composition.

[0155] The group (D.5) of the lubricants and leveling agents includes, for example, silicon-free but also silicon-containing polymers, for example polyacrylates or modified low molecular weight polydialkylsiloxanes. The modification consists in replacing some of the alkyl groups with a wide variety of organic radicals. These organic radicals are, for example, polyethers, polyesters or else long-chain alkyl radicals, the former finding most frequent use.

[0156] The polyether radicals of the correspondingly modified polysiloxanes are typically formed by means of ethylene oxide and/or propylene oxide units. The higher the proportion of these alkylene oxide units is in the modified polysiloxane, the more hydrophilic is generally the resulting product.

[0157] Such auxiliaries are obtainable commercially, for example, from Tego as TEGO® Glide 100, TEGO® Glide ZG 400, TEGO® Glide 406, TEGO® Glide 410, TEGO® Glide 411, TEGO® Glide 415, TEGO® Glide 420, TEGO® Glide 435, TEGO® Glide 440, TEGO® Glide 450, TEGO® Glide A 115, TEGO® Glide B 1484 (also usable as a defoamer and deaerating agent), TEGO® Flow ATF, TEGO® Flow ATF2, TEGO® Flow 300, TEGO® Flow 460, TEGO® Flow 425 and TEGO® Flow ZFS 460. The radiation-curable lubricants and leveling agents used, which additionally also serve to improve scratch resistance, can be the products TEGO® Rad 2100, TEGO® Rad 2200, TEGO® Rad 2300, TEGO® Rad 2500, TEGO® Rad 2600, TEGO® Rad 2700 and TEGO® Twin 4000, likewise obtainable from Tego. Such auxiliaries are obtainable from BYK, for example as BYK®-300, BYK®-306, BYK®-307, BYK®-310, BYK®-320, BYK®-322, BYK®-331, BYK®-333, BYK®-337, BYK®-341, Byk® 354, Byk® 361 N, BYK®-378 and BYK®-388.

[0158] The auxiliaries of group (D.5) are typically used in a proportion of from about 0.005 to 1.0% by weight, preferably from about 0.01 to 0.2% by weight, based on the total weight of the composition.

[0159] Group (D.6) includes, as radiation-curing auxiliaries, in particular polysiloxanes with terminal double bonds which are, for example, part of an acrylate group. Such auxiliaries can be made to crosslink by actinic or, for example, electron beam radiation. These auxiliaries generally combine several properties in one. In the uncrosslinked state, they can act as defoamers, deaerating agents, lubricants and leveling agents and/or substrate wetting aids; in the crosslinked state, they increase in particular the scratch resistance, for example of articles which can be produced with the inventive compositions. The improvement in the shine performance, for example, articles can essentially be regarded as the effect of the action of these auxiliaries as defoamers, devolatilizers and/or lubricants and leveling agents (in the uncrosslinked state). The radiation-curing auxiliaries which can be used are, for example, the products TEGO® Rad 2100, TEGO® Rad 2200, TEGO® Rad 2500, TEGO® Rad 2600 and TEGO® Rad 2700 obtainable from Tego, and the product BYK®-371 obtainable from BYK. Thermally curing auxiliaries of group (D.6) comprise, for example, primary OH groups which can react with isocyanate groups.

[0160] The thermally curing auxiliaries used can, for example, be the products BYK®-370, BYK®-373 and BYK®-375 obtainable from BYK. The auxiliaries of group (D.6) are typically used in a proportion of from about 0.1 to 5.0% by weight, preferably from about 0.1 to 3.0% by weight, based on the total weight of the composition.

[0161] The auxiliaries of group (D.7) of the substrate wetting aids serve in particular to increase the wettability of the substrate, which is to be imprinted or coated, for instance, by printing inks or coating compositions, for example compositions (a.1) to (a.5). The generally associated improvement in the lubricating and leveling performance of such printing inks or coating compositions has an effect on the appearance of the finished (for example crosslinked) print or of the finished (for example crosslinked) layer. A wide variety of such auxiliaries are commercially available, for example, from Tego as TEGO® Wet KL 245, TEGO® Wet 250, TEGO® Wet 260 and TEGO® Wet ZFS 453, and from BYK as BYK®-306, BYK®-307, BYK®-310, BYK®-333, BYK®-344, BYK®-345, BYK®-346 and Byk®-348.

[0162] Also very suitable are the products of the Zonyl® brand from Dupont, such as Zonyl® FSA and Zonyl® FSG. These are fluorinated surfactants/wetting agents.

[0163] The auxiliaries of group (D.7) are typically used in a proportion of from about 0.01 to 3.0% by weight, preferably from about 0.01 to 1.5% by weight and especially from 0.03 to 1.5% by weight, based on the total weight of the composition.

[0164] The auxiliaries of group (D.8) of the wetting and dispersing aids serve in particular to prevent the leaching and floating and also the settling of pigments, and are therefore useful, if necessary, in pigmented compositions in particular.

[0165] These auxiliaries stabilize pigment dispersions essentially by electrostatic repulsion and/or steric hindrance of the additized pigment particles, the interaction of the auxiliary with the surrounding medium (for example binder) playing

a major role in the latter case.

[0166] Since the use of such wetting and dispersing aids is common practice, for example, in the technical field of printing inks and paints, the selection of such a suitable auxiliary in the given case generally presents no difficulties to the person skilled in the art.

[0167] Such wetting and dispersing aids are supplied commercially, for example, by Tego as TEGO® Dispers 610, TEGO® Dispers 610 S, TEGO® Dispers 630, TEGO® Dispers 700, TEGO® Dispers 705, TEGO® Dispers 710, TEGO® Dispers 720 W, TEGO® Dispers 725 W, TEGO® Dispers 730 W, TEGO® Dispers 735 W and TEGO® Dispers 740 W, and by BYK as Disperbyk®, Disperbyk®-107, Disperbyk®-108, Disperbyk®-110, Disperbyk®-111, Disperbyk®-115, Disperbyk®-130, Disperbyk®-160, Disperbyk®-161, Disperbyk®-162, Disperbyk®-163, Disperbyk®-164, Disperbyk®-165, Disperbyk®-166, Disperbyk®-167, Disperbyk®-170, Disperbyk®-174, Disperbyk®-180, Disperbyk®-181, Disperbyk®-182, Disperbyk®-183, Disperbyk®-184, Disperbyk®-185, Disperbyk®-190, Anti-Terra®-U, Anti-Terra®-U 80, Anti-Terra®-P, Anti-Terra®-203, Anti-Terra®-204, Anti-Terra® 5 206, BYK®-151, BYK®-154, BYK®-155, BYK®-P 104 S, BYK®-P 105, Lactimon®, Lactimon®-WS and Bykumen®. The abovementioned Zonyl® brands, such as Zonyl® FSA and Zonyl® FSG, from DuPont are also useful here.

[0168] The dosage of the auxiliaries of group (D.8) depends mainly upon the surface area of the pigments to be covered and upon the mean molar mass of the auxiliary.

[0169] For inorganic pigments and low molecular weight auxiliaries, a content of the latter of from about 0.5 to 2.0% by weight based on the total weight of pigment and auxiliary is typically assumed. In the case of high molecular weight auxiliaries, the content is increased to from about 1.0 to 30% by weight.

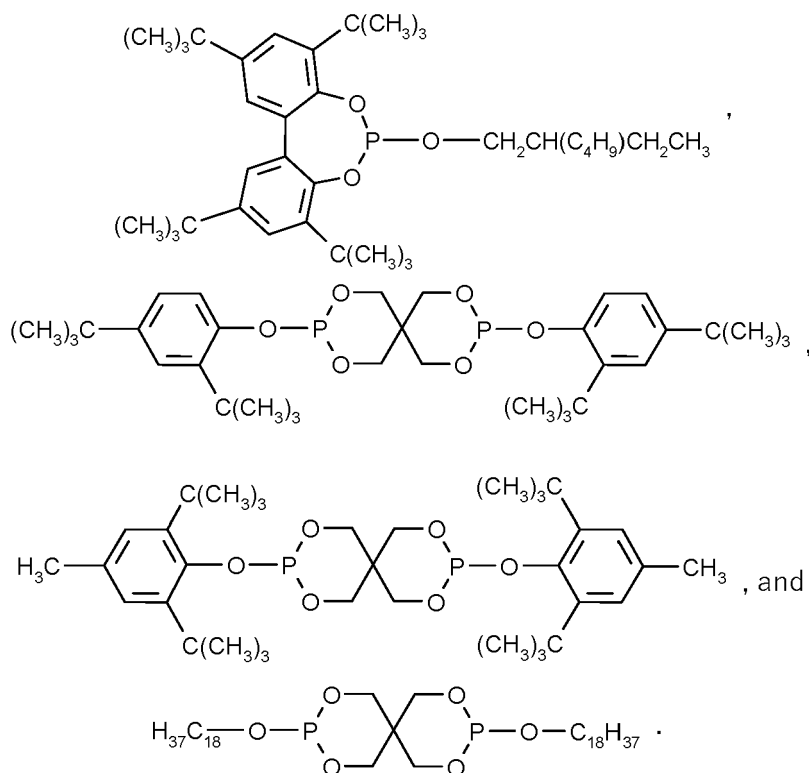
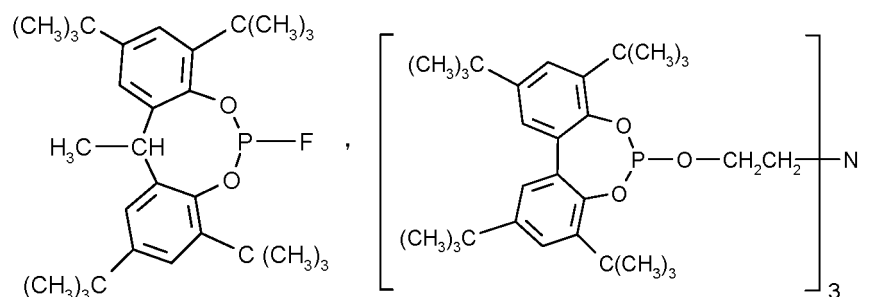
[0170] In the case of organic pigments and low molecular weight auxiliaries, the content of the latter is from about 1.0 to 5.0% by weight based on the total weight of pigment and auxiliary. In the case of high molecular weight auxiliaries, this content may be in the range from about 10.0 to 90% by weight. In every case, therefore, preliminary experiments are recommended, which can, though, be accomplished by the person skilled in the art in a simple manner.

[0171] The hydrophobizing agents of group (D.9) can be used with a view, for example, to providing articles obtained with inventive compositions with water-repellent properties. This means that swelling resulting from water absorption and hence a change, for example, in the optical properties of such articles is no longer possible or at least greatly suppressed. In addition, when the compositions are used, for example, as a printing ink in 3D printing, their absorption of water can be prevented or at least greatly inhibited. Such hydrophobizing agents are commercially available, for example, from Tego as Tego® Phobe WF, Tego® Phobe 1000, Tego® Phobe 1000 S, Tego® Phobe 1010, Tego® Phobe 1030, Tego® Phobe 1040, Tego® Phobe 1050, Tego® Phobe 1200, Tego® Phobe 1300, Tego® Phobe 1310 and Tego® Phobe 1400.

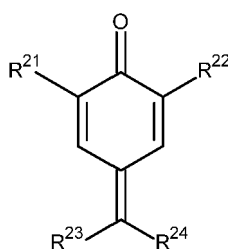
[0172] The auxiliaries of group (D.9) are used typically in a proportion of from about 0.05 to 5.0% by weight, preferably from about 0.1 to 3.0% by weight, based on the total weight of the composition.

[0173] In-can stabilizers of group (D.10) provide increased storage stability from manufacturing to curing. Examples of in-can stabilizers of group (D.10) are:

Phosphites and phosphonites (processing stabilizer), for example triphenyl phosphite, diphenylalkyl phosphites, phenyldialkyl phosphites, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,4-di-cumylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite, diisodecyloxy pentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl) pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylene diphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenz[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl)methyl phosphite, bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenz[d,g]-1,3,2-dioxaphosphocin, 2,2',2''-nitrido[triethyltris(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite], 2-ethylhexyl(3,3',5,5'-tetra-tert-butyl-1,1'-biphenyl-2,2'-diyl)phosphite, 5-butyl-5-ethyl-2-(2,4,6-tri-tert-butylphenoxy)-1,3,2-dioxaphosphirane, phosphorous acid, mixed 2,4-bis(1,1-dimethylpropyl)phenyl and 4-(1,1-dimethylpropyl)phenyl triesters (CAS No. 939402-02-5), Phosphorous acid, triphenyl ester, polymer with alpha-hydro-omega-hydroxypoly[oxy(methyl-1,2-ethanediyl)], C10-16 alkyl esters (CAS No. 1227937-46-3). The following phosphites are especially preferred: Tris(2,4-di-tert-butylphenyl) phosphite, tris(nonylphenyl) phosphite,



[0174] Quinone methides of the formula

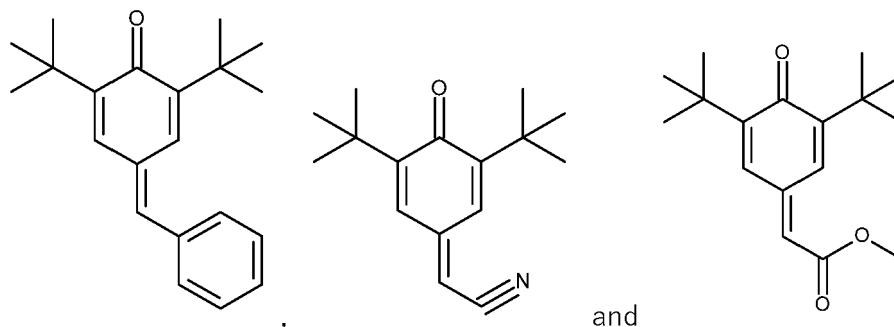


(providing long term shelf life stability), wherein

R²¹ and R²² independently of each other are C₁-C₁₈alkyl, C₅-C₁₂cycloalkyl, C₇-C₁₅-phenylalkyl, optionally substituted C₆-C₁₀aryl;

R²³ and R²⁴ independently of each other are H, optionally substituted C₆-C₁₀-aryl, 2-,3-,4-pyridyl, 2-,3-furyl or thienyl, COOH, COOR²⁵, CONH₂, CONHR²⁵, CONR²⁵R²⁶, -CN, -COR²⁵, -OCOR²⁵, -OPO(OR²⁵)₂, wherein R²⁵ and R²⁶ are independently of each other C₁-C₈alkyl, or phenyl. Quinone methides are preferred, wherein R²¹ and R²² are tert-butyl;

R²³ is H, and R²⁴ is optionally substituted phenyl, COOH, COOR²⁵, CONH₂, CONHR²⁵, CONR²⁵R²⁶, -CN, -COR²⁵, -OCOR²⁵, -OPO(OR²⁵)₂, wherein R²⁵ and R²⁶ are C₁-C₈alkyl, or phenyl. Examples of quinone methides are



[0175] The quinone methides may be used in combination with highly sterically hindered nitroxyl radicals as described, for example, in US20110319535.

[0176] In-can stabilizers of group (D.10) are used typically in a proportion of from about 0.01 to 0.3% by weight, preferably from about 0.04 to 0.15% by weight, based on the total weight of the composition.

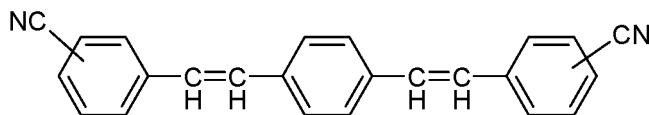
[0177] The group (D.11) of the auxiliaries for improving scratch resistance includes, for example, the products TEGO® Rad 2100, TEGO® Rad 2200, TEGO® Rad 2500, TEGO® Rad 2600 and TEGO® Rad 2700 which are obtainable from Tego and have already been mentioned above.

[0178] For these auxiliaries, useful amounts are likewise those mentioned in group (D.6), i.e. these additives are typically used in a proportion of from about 0.1 to 5.0% by weight, preferably from about 0.1 to 3.0% by weight, based on the total weight of the composition.

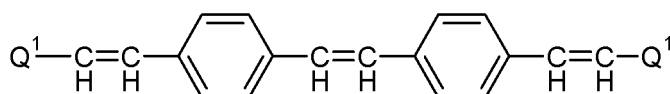
[0179] The group (E.1) of the dyes includes, for example, dyes from the class of the azo dyes, metal complex dyes, basic dyes such as di- and triarylmethane dyes and salts thereof, azomethine derivatives, polymethines, anthraquinone dyes and the like. An overview of suitable dyes which can be used in the inventive composition is given by the book by H. Zollinger, "Color Chemistry", Wiley-VCH, Weinheim, 3rd edition 2003.

[0180] It is in particular also possible to add to the inventive compositions photochromic, thermochromic or luminescent dyes, and dyes which have a combination of these properties. In addition to the typical fluorescent dyes, fluorescent dyes should also be understood to mean optical brighteners. Optical brighteners may be used for the optimization of the absorption characteristics (critical energy and depth of penetration) of the photocurable composition.

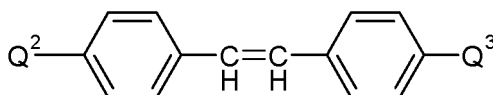
[0181] Examples of the latter include the class of the bisstyrylbenzenes, especially of the cyanostyryl compounds, and correspond to the formula



[0182] Further suitable optical brighteners from the class of the stilbenes are, for example, those of the formulae

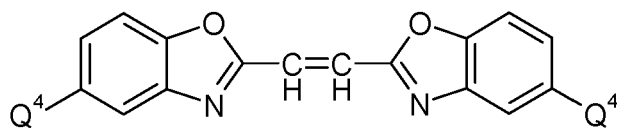


and

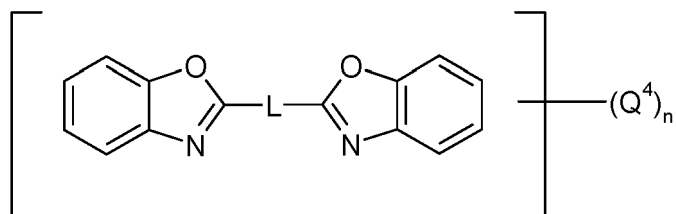


in which Q¹ is in each case C₁-C₄-alkoxycarbonyl or cyano, Q² is benzoxazol-2-yl, which may be mono- or disubstituted by C₁-C₄-alkyl, especially methyl, Q³ is C₁-C₄-alkoxycarbonyl or 3-(C₁-C₄-alkyl)-1,2,4-oxadiazol-3-yl.

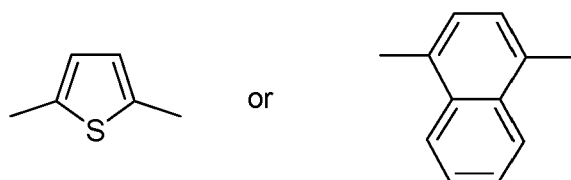
[0183] Further suitable optical brighteners from the class of the benzoxazoles obey, for example, the formulae



or

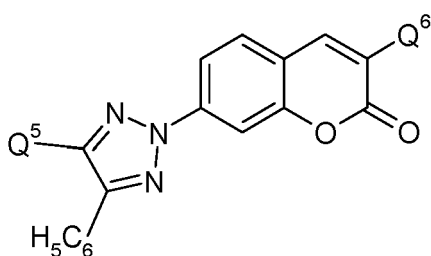


in which Q^4 is in each case C_1 - C_4 -alkyl, especially methyl, L is a radical of the formula



and n is an integer from 0 to 2.

[0184] Suitable optical brighteners from the class of the coumarins have, for example, the formula

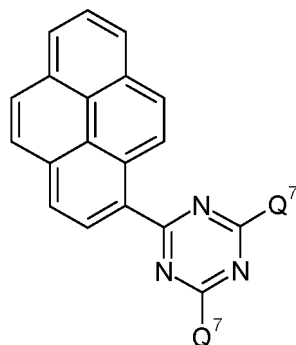


in which

Q^5 is C_1 - C_4 -alkyl and

Q^6 is phenyl or 3-halopyrazol-1-yl, especially 3-chloropyrazol-1-yl.

[0185] Further suitable optical brighteners from the class of the pyrenes correspond, for example, to the formula



in which

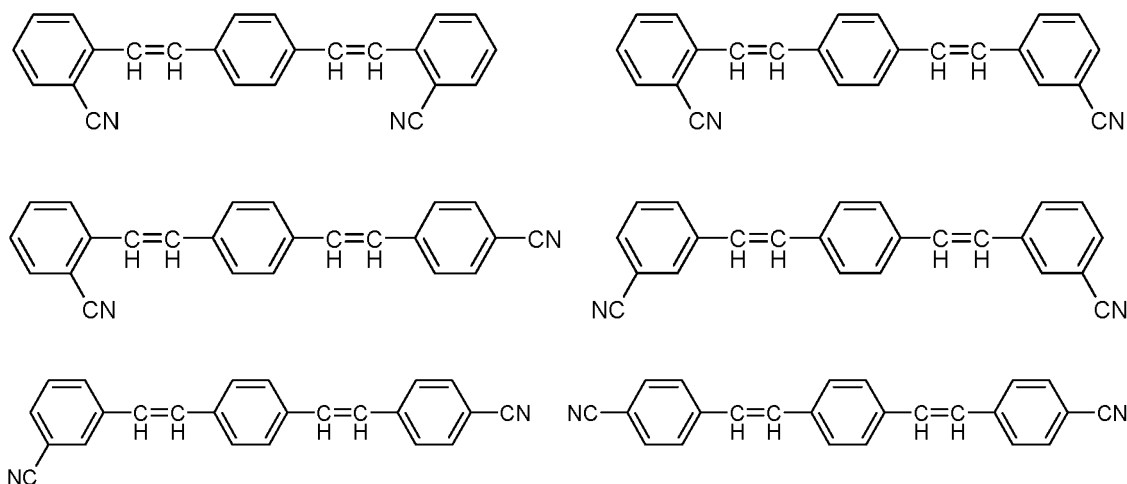
Q⁷ is in each case C₁-C₄-alkoxy, especially methoxy.

[0186] The abovementioned brighteners can be used either alone or in a mixture with one another.

[0187] The abovementioned optical brighteners are generally commercially available products known per se. They are described, for example, in Ullmann's Encyclopedia of Industrial Chemistry, 5th edition, volume A18, pages 156 to 161, or can be obtained by the methods described there.

[0188] In particular, if desired, one or more optical brighteners from the class of the bisstyrylbenzenes is used, especially of the cyanostyrylbenzenes. The latter may be used as individual compounds, but also as a mixture of the isomeric compounds.

[0189] In this case, the isomers correspond to the formulae



[0190] Optical brighteners are sold, for example, commercially as Ultraphor® SF 004, Ultraphor® SF MO, Ultraphor® SF MP and Ultraphor® SF PO from BASF SE.

[0191] The group (E.2) of the pigments includes both inorganic and organic pigments. An overview of inorganic colored pigments which can be used in the inventive compositions is given by the book by H. Endriß "Aktuelle anorganische Bunt-Pigmente" ["Current inorganic colored pigments"] (publisher U. Zorll, Curt-R.-Vincentz-Verlag Hanover 1997), and the book by G. Buxbaum, "Industrial Inorganic Pigments", Wiley-VCH, Weinheim, 3rd edition 2005. In addition, useful further pigments which are not listed in the aforementioned book are also Pigment Black 6 and Pigment Black 7 (carbon black), Pigment Black 11 (iron oxide black, Fe₃O₄), Pigment White 4 (zinc oxide, ZnO), Pigment White 5 (lithopone, ZnS/BaSO₄), Pigment White 6 (titanium oxide, TiO₂) and Pigment White 7 (zinc sulfide, ZnS).

[0192] An overview of organic pigments which can be added to the inventive compositions is provided by the book by W. Herbst and K. Hunger "Industrielle organische Pigmente" ["Industrial Organic Pigments"], Wiley-VCH, Weinheim, 3rd edition 2004.

[0193] It is also possible to add to the inventive compositions magnetic, electrically conductive, photochromic, thermochromic or luminescent pigments, and also pigments which have a combination of these properties.

[0194] In addition to some organic pigments, for example Lumogen® Yellow 0795 (BASF SE), useful pigments having luminescent properties are also inorganic, doped or undoped compounds essentially based on alkaline earth metal oxides, alkaline earth metal/transition metal oxides, alkaline earth metal/aluminum oxides, alkaline earth metal/silicon oxides or alkaline earth metal/phosphorus oxides, alkaline earth metal halides, Zn/silicon oxides, Zn/alkaline earth metal halides, rare earth metal oxides, rare earth metal/transition metal oxides, rare earth metal/aluminum oxides, rare earth metal/silicon oxides or rare earth metal/phosphorus oxides, rare earth metal oxide sulfides or oxide halides, zinc oxide, sulfide or selenide, cadmium oxide, sulfide or selenide or zinc/cadmium oxide, sulfide or selenide, the cadmium compounds being of lower importance owing to their toxicological and ecological relevance.

[0195] The dopants used in these compounds are usually aluminum, tin, antimony, rare earth metals, such as cerium, europium or terbium, transition metals, such as manganese, copper, silver or zinc, or combinations of these elements.

[0196] Luminescent pigments are specified below by way of example, the notation "compound:element(s)" being taken to mean to the relevant person skilled in the art that said compound has been doped with the corresponding element(s). In addition, for example, the notation "(P,V)", denotes that the corresponding lattice positions in the solid structure of the pigment are randomly occupied by phosphorus and vanadium.

[0197] Examples of such compounds which are capable of luminescence are MgWO_4 , CaWO_4 , $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}$, $\text{BaMg}_2\text{Al}_{10}\text{O}_{27}:\text{Eu}$, $\text{MgAl}_{11}\text{O}_{19}:\text{Ce,Tb}$, $\text{MgSiO}_3:\text{Mn}$, $\text{Ca}_{10}(\text{PO}_4)_6(\text{F,Cl}):\text{Sb,Mn}$, $(\text{SrMg})_2\text{P}_2\text{O}_7:\text{Eu}$, $\text{SrMg}_2\text{P}_2\text{O}_7:\text{Sn}$, $\text{BaFCl}:\text{Eu}$, $\text{Zn}_2\text{SiO}_4:\text{Mn}$, $(\text{Zn,Mg})\text{F}_2:\text{Mn}$, $\text{Y}_2\text{O}_3:\text{Eu}$, $\text{YVO}_4:\text{Eu}$, $\text{Y}(\text{P,V})\text{O}_4:\text{Eu}$, $\text{Y}_2\text{SiO}_5:\text{Ce,Tb}$, $\text{Y}_2\text{O}_2\text{S}:\text{Eu}$, $\text{Y}_{22}\text{S}:\text{Tb}$, $\text{La}_2\text{O}_2\text{S}:\text{Tb}$, $\text{Gd}_2\text{O}_2\text{S}:\text{Tb}$, $\text{LaOBr}:\text{Tb}$, $\text{ZnO}:\text{Zn}$, $\text{ZnS}:\text{Mn}$, $\text{ZnS}:\text{Ag}$, $\text{ZnS/CdS}:\text{Ag}$, $\text{ZnS}:\text{Cu,Al}$, $\text{ZnSe}:\text{Mn}$, $\text{ZnSe}:\text{Ag}$ and $\text{ZnSe}:\text{Cu}$.

[0198] Examples of light, heat and/or oxidation stabilizers as component F include:

alkylated monophenols, such as 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethylphenol, 2,6-di-tert-butyl-4-n-butylphenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclopentyl-4-methylphenol, 2-(α -methylcyclohexyl)-4,6-dimethylphenol, 2,6-dioctadecyl-4-methylphenol, 2,4,6-tricyclohexylphenol, 2,6-di-tert-butyl-4-methoxymethylphenol, nonylphenols which have a linear or branched side chain, for example 2,6-dinonyl-4-methylphenol, 2,4-dimethyl-6-(1'-methylundec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methylheptadec-1'-yl)phenol, 2,4-dimethyl-6-(1'-methyltridec-1'-yl)phenol and mixtures of these compounds, alkylthiomethylphenols, such as 2,4-dioctylthiomethyl-6-tert-butylphenol, 2,4-dioctylthiomethyl-6-methylphenol, 2,4-dioctylthiomethyl-6-ethylphenol and 2,6-didodecylthiomethyl-4-nonylphenol, hydroquinones and alkylated hydroquinones, such as 2,6-di-tert-butyl-4-methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-diphenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenyl stearate and bis(3,5-di-tert-butyl-4-hydroxyphenyl)adipate, tocopherols, such as α -tocopherol, β -tocopherol, γ -tocopherol, δ -tocopherol and mixtures of these compounds, and tocopherol derivatives, such as tocopheryl acetate, succinate, nicotinate and polyoxyethylenesuccinate ("tocopherolate"), hydroxylated diphenyl thioethers, such as 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4-octylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-di-sec-amylphenol) and 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl) disulfide, alkylidenebisphenols, such as 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4-ethylphenol), 2,2'-methylenebis[4-methyl-6-(α -methylcyclohexyl)phenol], 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,2'-methylenebis(6-nonyl-4-methylphenol), 2,2'-methylenebis(4,6-di-tert-butylphenol), 2,2-ethylidenebis(4,6-di-tert-butylphenol), 2,2'-ethylidenebis(6-tert-butyl-4-isobutylphenol), 2,2'-methylenebis[6-(α -methylbenzyl)-4-nonylphenol], 2,2'-methylenebis[6-(α , α -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenebis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl) butane, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1,3-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)butane, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-tert-butyl-4'-hydroxyphenyl)butyrate], bis(3-tert-butyl-4-hydroxy-5-methylphenyl)dicyclopentadiene, bis[2-(3'-tert-butyl-2'-hydroxy-5'-methylbenzyl)-6-tert-butyl-4-methylphenyl] terephthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)butane, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-n-dodecylmercaptobutane and 1,1,5,5-tetrakis(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane, O-, N- and S-benzyl compounds, such as 3,5,3',5'-tetra-tert-butyl-4,4'-dihydroxydibenzyl ether, octadecyl 4-hydroxy-3,5-dimethylbenzylmercaptoacetate, tridecyl 4-hydroxy-3,5-di-tert-butyl benzyl mercaptoacetate, tris(3,5-di-tert-butyl-4-hydroxybenzyl)amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) dithioterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl) sulfide and isooctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate, aromatic hydroxybenzyl compounds, such as 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethyl benzene and 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol, triazine compounds, such as 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyanilino)-1,3,5-triazine, 2-octylmercapto-4,6-bis(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxy)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) isocyanurate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylethyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxyphenyl propionyl)hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl) isocyanurate and 1,3,5-tris(2-hydroxyethyl) isocyanurate, benzylphosphonates, such as dimethyl 2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl 3,5-di-tert-butyl-4-hydroxybenzylphosphonate and dioctadecyl 5-tert-butyl-4-hydroxy-3-methylbenzylphosphonate, acylaminophenols, such as 4-hydroxylauroylanilide, 4-hydroxystearoylanilide and octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate, propionic and acetic esters, for example of monohydric or polyhydric alcohols, such as methanol, ethanol, n-octanol, isooctanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentaerythritol, tris(hydroxyethyl) isocyanurate, N,N'-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylhexanediol, trimethylolpropane and 4-hydroxymethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane, propionamides based on amine derivatives, such as N,N'-

bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexamethylenediamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethylenediamine and N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine, ascorbic acid (Vitamin C) and ascorbic acid derivatives, such as ascorbyl palmitate, laurate and stearate, and ascorbyl sulfate and phosphate,

antioxidants based on amine compounds, such as N,N'-diisopropyl-p-phenylenediamine, N,N'-di-sec-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-methylheptyl)-p-phenylenediamine, N,N'-dicyclohexyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylheptyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfamoyl)diphenylamine, N,N'-dimethyl-N,N'-di-sec-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octyl-substituted diphenylamine, such as p,p'-di-tert-octyldiphenylamine, 4-n-butylaminophenol, 4-butyrylamino-phenol, 4-nonanoylamino-phenol, 4-dodecanoylamino-phenol, 4-octadecanoylamino-phenol, bis[4-methoxyphenyl]amine, 2,6-di-tert-butyl-4-dimethylaminomethylphenol, 2,4-diaminodiphenylmethane, 4,4'-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenyl methane, 1,2-bis[(2-methylphenyl)amino]ethane, 1,2-bis(phenylamino)propane, (o-tolyl)biguanide, bis[4-(1',3'-dimethylbutyl)phenyl]amine, tert-octyl-substituted N-phenyl-1-naphthylamine, a mixture of mono- and dialkylated tert-butyl/tert-octyldiphenylamine, a mixture of mono- and dialkylated nonyldiphenylamine, a mixture of mono- and dialkylated dodecyldiphenylamine, a mixture of mono- and dialkylated isopropyl/isoheptyldiphenylamine, a mixture of mono- and dialkylated tert-butyl/tert-octylphenothiazine, a mixture of mono- and dialkylated tert-octylphenothiazine, N-allylphenothiazine, N,N,N',N'-tetraphenyl-1,4-diaminobut-2-ene, N,N-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine, bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate, 2,2,6,6-tetramethylpiperidin-4-one and 2,2,6,6-tetramethylpiperidin-4-ol,

phosphites and phosphonites, such as triphenylphosphite, diphenyl alkyl phosphite, phenyl dialkyl phosphite, tris(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, distearyl pentaerythritol diphosphite, tris(2,4-di-tert-butylphenyl) phosphite, diisodecyl pentaerythritol diphosphite, bis(2,4-di-tert-butylphenyl) pentaerythritol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl) pentaerythritol diphosphite, diisodecyloxy pentaerythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) pentaerythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl)) pentaerythritol diphosphite, tristearyl sorbitol triphosphite, tetrakis(2,4-di-tert-butylphenyl) 4,4'-biphenylenediphosphonite, 6-isooctyloxy-2,4,8,10-tetra-tert-butyl-12H-dibenzo[d,g]-1,3,2-dioxaphosphocine, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenzo[d,g]-1,3,2-dioxaphosphocine, bis(2,4-di-tert-butyl-6-methylphenyl) methyl phosphite and bis(2,4-di-tert-butyl-6-methylphenyl) ethyl phosphite,

2-(2'-hydroxyphenyl)benzotriazoles, such as 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-5'-(1,1,3,3-tetramethylbutyl)phenyl)benzotriazole, 2-(3',5'-di-tert-butyl-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-methylphenyl)-5-chlorobenzotriazole, 2-(3'-sec-butyl-5'-tert-butyl-2'-hydroxyphenyl)benzotriazole, 2-(2'-hydroxy-4'-octyloxyphenyl)benzotriazole, 2-(3',5'-di-tert-amyl-2'-hydroxyphenyl)benzotriazole, 2-(3',5'-bis(a,a-dimethylbenzyl)-2'-hydroxyphenyl)benzotriazole, a mixture of 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxy-carbonyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonyl]ethyl)-2'-hydroxyphenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-methoxycarbonyl)ethyl)phenyl)-5-chlorobenzotriazole, 2-(3'-tert-butyl-2'-hydroxy-5'-(2-octyloxy-carbonyl)ethyl)phenyl)benzotriazole, 2-(3'-tert-butyl-5'-[2-(2-ethylhexyloxy)carbonyl]ethyl)-2'-hydroxyphenyl)benzotriazole, 2-(3'-dodecyl-2'-hydroxy-5'-methylphenyl)benzotriazole and 2-(3'-tert-butyl-2'-hydroxy-5'-(2-isooctyloxy-carbonyl)ethyl)phenyl)benzotriazole, 2,2'-methylenebis[4-(1,1,3,3-tetramethylbutyl)-6-benzotriazol-2-ylphenol]; the product of complete esterification of 2-[3'-tert-butyl-5'-(2-methoxycarbonyl)ethyl]-2'-hydroxyphenyl]-2H-benzotriazole with polyethylene glycol 300; $[R-CH_2CH_2-COO(CH_2)_3]_2$, where $R = 3'$ -tert-butyl-4'-hydroxy-5'-2H-benzotriazol-2-ylphenyl],

sulfur-containing peroxide scavengers and sulfur-containing antioxidants, such as esters of 3,3'-thiodipropionic acid, for example the lauryl, stearyl, myristyl and tridecyl esters, mercaptobenzimidazole and the zinc salt of 2-mercaptobenzimidazole, dibutylzinc dithiocarbamate, dioctadecyl disulfide and pentaerythritol tetrakis((β-dodecyl mercapto)propionate),

2-hydroxybenzophenones, such as the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzyloxy, 4,2',4'-trihydroxy and 2'-hydroxy-4,4'-dimethoxy derivatives, esters of unsubstituted and substituted benzoic acids, such as 4-tert-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoylresorcinol, bis(4-tert-butylbenzoyl)resorcinol, benzoylresorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate, hexadecyl-3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl-3,5-di-tert-butyl-4-hydroxybenzoate and 2-methyl-4,6-di-tert-butylphenyl-3,5-di-tert-butyl-4-hydroxybenzoate,

acrylates, such as ethyl α -cyano- β , β -diphenylacrylate, isooctyl α -cyano- β , β -diphenylacrylate, methyl α -methoxycarbonylcinnamate, methyl α -cyano- β -methyl-p-methoxycinnamate, butyl- α -cyano- β -methyl-p-methoxycinnamate and methyl- α -methoxycarbonyl-p-methoxycinnamate,

sterically hindered amines, such as bis(2,2,6,6-tetramethylpiperidin-4-yl) sebacate, bis(2,2,6,6-tetramethylpiperidin-4-yl) succinate, bis(1,2,2,6,6-pentamethylpiperidin-4-yl) sebacate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate, bis(1,2,2,6,6-pentamethylpiperidin-4-yl)-n-butyl-3,5-di-tert-butyl-4-hydroxybenzylmalonate, the condensation product of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, the condensation product of N,N'-bis(2,2,6,5-tetramethylpiperidin-4-yl)hexamethylenediamine and 4-tert-octylamino-2,6-dichloro-1,3,5-triazine, tris(2,2,6,6-tetramethylpiperidin-4-yl) nitrilotriacetate, tetrakis(2,2,6,6-tetramethylpiperidin-4-yl) 1,2,3,4-butanetetracarboxylate, 1,1'-(1,2-ethylene)bis(3,3,5,5-tetramethylpiperazinone), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearyloxy-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethylpiperidin-4-yl) 2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)malonate, 3-n-octyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, bis(1-octyloxy-2,2,6,6-tetramethylpiperidin-4-yl) sebacate, bis(1-octyloxy-2,2,6,5-tetramethylpiperidin-4-yl) succinate, the condensation product of N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensation product of 2-chloro-4,6-bis(4-n-butylamino-2,2,6,6-tetramethylpiperidin-4-yl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensation product of 2-chloro-4,6-di(4-n-butylamino-1,2,2,6,6-pentamethylpiperidin-4-yl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triazaspiro[4.5]decane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethylpiperidin-4-yl)pyrrolidine-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethylpiperidin-4-yl)pyrrolidine-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearyloxy-2,2,6,6-tetramethylpiperidine, the condensation product of N,N'-bis(2,2,6,6-tetramethylpiperidin-4-yl)hexamethylenediamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, the condensation product of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine, 4-butylamino-2,2,6,6-tetramethylpiperidine, N-(2,2,6,6-tetramethylpiperidin-4-yl)-n-dodecylsuccinimide, N-(1,2,2,6,6-pentamethylpiperidin-4-yl)-n-dodecylsuccinimide, 2-undecyl-7,7,9,9-tetramethyl-1-oxa-3,8-diaza-4-oxo-spiro[4.5]decane, the condensation product of 7,7,9,9-tetramethyl-2-cycloundecyl-1-oxa-3,8-diaza-4-oxospiro[4.5]decane and epichlorohydrin, the condensation products of 4-amino-2,2,6,6-tetramethylpiperidine with tetramethylolacetylenediureas and poly(methoxypropyl-3-oxo)-[4(2,2,6,6-tetramethyl)piperidinyl]siloxane, oxamides, such as 4,4'-dioctyloxyoxanilide, 2,2'-diethoxyoxanilide, 2,2'-dioctyloxy-5,5'-di-tert-butoxanilide, 2,2'-didodecyloxy-5,5'-di-tert-butoxanilide, 2-ethoxy-2'-ethyloxanilide, N,N'-bis(3-dimethylaminopropyl)oxamide, 2-ethoxy-5-tert-butyl-2'-ethoxanilide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxanilide, and mixtures of ortho-, para-methoxy-disubstituted oxanilides and mixtures of ortho- and para-ethoxy-disubstituted oxanilides, and 2-(2-hydroxyphenyl)-1,3,5-triazines, such as 2,4,6-tris-(2-hydroxy-4-octyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2,4-dihydroxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4-bis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-bis(4-methyl-5 phenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecyloxyphenyl)-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butyloxypropoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-octyloxypropoxy)phenyl]-4,6-bis(2,4-dimethyl)-1,3,5-triazine, 2-[4-(dodecyloxy/tridecyloxy-2-hydroxypropoxy)-2-hydroxyphenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecyloxypropoxy)phenyl]-4,6-bis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2-(2-hydroxy-4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine, 2,4,6-tris[2-hydroxy-4-(3-butoxy-2-hydroxypropoxy)phenyl]-1,3,5-triazine and 2-(2-hydroxyphenyl)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine.

[0199] The components G of the IR absorber used are compounds which exhibit one or more absorption bands in the infrared spectral region, i.e. from > 750 nm, e.g. from 751 nm, to 1 mm. Preference is given to compounds which exhibit one absorption band in the near infrared (NIR) spectral region, i.e. from > 750 (e.g. 751) to 2000 nm, and optionally additionally also in the visible spectral region, especially from 550 to 750 nm. When the compounds absorb both in the IR and in the visible spectral region, they preferably exhibit the greatest absorption maximum in the IR region and a smaller maximum (frequently in the form of a so-called absorption shoulder) in the visible region. In a particular embodiment, the compounds of component G additionally also exhibit fluorescence. Fluorescence is the transition of a system excited by absorption of electromagnetic radiation (usually visible light, UV radiation, X-rays or electron beams) to a state of lower energy by spontaneous emission of radiation of the same wavelength (resonance fluorescence) or longer wavelength. Preferred compounds of component G exhibit, when they fluoresce, a fluorescence in the IR spectral region, preferably in the NIR.

[0200] Such compounds are, for example, selected from naphthalenes, anthracenes, phenanthrenes, tetracenes, perylenes, terrylenes, quaterrylenes, pentarylenes, hexarylenes, anthraquinones, indanthrones, acridines, carbazoles, dibenzofuranes, dinaphthofuranes, benzimidazoles, benzthiazoles, phenazines, di-oxazines, quinacridones, metal phthalocyanines, metal naphthalocyanines, metal porphyrines, coumarines, dibenzofuranones, dinaphthofuranones,

benzimidazolones, indigo compounds, thioindigo compounds, quinophthalones, naphthoquinophthalones and diketo-pyrrolopyrroles. Particularly preferred compounds of component G which absorb IR radiation and optionally fluoresce are selected from naphthalenes, anthracenes, phenanthrenes, tetracenes, perylenes, terrylenes, quaterrylenes, pentarylenes and hexarylenes, more preferably from perylenes, terrylenes and quaterrylenes and especially from terrylenes and quaterrylenes. The compound is especially a quaterrylene. Suitable compounds are described in WO 2008/012292.

[0201] The present disclosure(s) also provides methods suitable for making 3-dimensional structures comprising a plurality of polymer layers and 3-dimensional patterns.

[0202] Some embodiments provide methods of patterning a polymeric image on a substrate, each method comprising;

- (a) depositing a layer of photocurable composition of any one of the compositions described herein on the substrate;
- (b) irradiating a portion of the layer of photocurable composition with a light having appropriate wavelength(s), thereby providing a patterned layer of polymerized and unpolymerized regions. Certain other embodiments further comprise removing the unpolymerized region of the pattern.

[0203] The method may comprise depositing a plurality of layers of a photocurable composition on a substrate before irradiation, at least one of which is the photocurable composition used according to the present invention.

[0204] The irradiated portion is patterned through use of a photomask, by a direct writing application of light, by interference, nanoimprint, or diffraction gradient lithography, by inkjet 3D printing, stereolithography, holography, LCD or digital light projection (DLP). The photocurable compositions may be irradiated by any variety of methods known in the art. Patterning may be achieved by photolithography, using a positive or negative image photomask, by interference lithography (i.e., using a diffraction grating), by proximity field nanopatterning by diffraction gradient lithography, or by a direct laser writing application of light, such as by multi-photon lithography, by nanoimprint lithography, by inkjet 3D printing, stereolithography and the digital micromirror array variation of stereolithography (commonly referred to as digital light projection (DLP)). The photocurable compositions are especially amenable to preparing structures using stereolithographic methods, for example including digital light projection (DLP). The photocurable compositions may be processed as bulk structures, for example using vat polymerization, wherein the photopolymer is cured directly onto a translated or rotated substrate, and the irradiation is patterned via stereolithography, holography, or digital light projection (DLP).

[0205] Stereolithography (SLA) is a form of three-dimensional (3D) printing technology used for creating models, prototypes, patterns and production parts in a layer by layer fashion (so-called "additive manufacturing") using photopolymerization, a process by which light causes chains of molecules to link, forming polymers. Those polymers then make up the body of a three-dimensional solid. Typically, an SLA additive manufacturing process uses a build platform having a build tray submerged in a liquid photosensitive material. A 3D model of the item to be manufactured is imported into an associated 3D printer software, which software slices the 3D model into 2D images that are then projected onto the build platform to expose the photopolymer.

[0206] FIG. 3 of US4575330 depicts a known prior art "top-down" approach to printing. A container 21 is filled with a UV curable liquid 22 or the like, to provide a designated working surface 23. A programmable source of ultraviolet (UV) light 26 produces a spot of ultraviolet light 27 in the plane of surface 23. The spot 27 is movable across the surface 23 by the motion of mirrors or other optical or mechanical elements that are a part of light source 26. The position of the spot 27 on surface 23 is controlled by a computer 28. A movable elevator platform 29 inside container 21 is moved up and down selectively, the position of the platform being controlled by the computer 28. The elevator platform may be driven mechanically, pneumatically, hydraulically or electrically, and it typically uses optical or electronic feedback to precisely control its position. As the device operates, it produces a three-dimensional object 30 by step-wise buildup of integrated laminate such as 30a, 30b, 30c. During this operation, the surface of the UV curable liquid 22 is maintained at a constant level in the container 21, and the spot of UV light 27 is moved across the working surface 23 in a programmed manner. As the liquid 22 cures and solid material forms, the elevator platform 29 that was initially just below surface 23 is moved down from the surface in a programmed manner by any suitable actuator. In this way, the solid material that was initially formed is taken below surface 23 and new liquid 22 flows across the surface 23. A portion of this new liquid is, in turn, converted to solid material by the programmed UV light spot 27, and the new material adhesively connects to the material below it. This process is continued until the entire three-dimensional object 30 is formed.

[0207] A computer controlled pump (not shown) may be used to maintain a constant level of the liquid 22 at the working surface 23. Appropriate level detection system and feedback networks can be used to drive a fluid pump or a liquid displacement device to offset changes in fluid volume and maintain constant fluid level at the surface 23. Alternatively, the source 26 can be moved relative to the sensed level 23 and automatically maintain sharp focus at the working surface 23. All of these alternatives can be readily achieved by conventional software operating in conjunction with the computer control system 28.

[0208] An alternative approach is to build the item from the "bottom-up" as depicted in FIG. 4 of US4575330. In this approach, the UV curable liquid 22 floats on a heavier UV transparent liquid 32 that is non-miscible and non-wetting

with the curable liquid 22. By way of example, ethylene glycol or heavy water are suitable for the intermediate liquid layer 32. In the system of FIG. 4, the three-dimensional object 30 is pulled up from the liquid 22, rather than down and further into the liquid medium, as shown in the system of FIG. 3. In particular, the UV light source 26 in FIG. 4 focuses the spot 27 at the interface between the liquid 22 and the non-miscible intermediate liquid layer 32, the UV radiation

passing through a suitable UV transparent window 33, of quartz or the like, supported at the bottom of the container 21. [0209] According to WO2018106977, and in lieu of printing just from resin in its liquid phase, one or more layers of the item are printed from resin that is foamed (at the build surface 23).

[0210] FIG. 3 of WO2018106977 depicts a representative implementation of an additive manufacturing method and apparatus wherein resin foam is the source material for the printer. A top-down printing method is depicted. In this example embodiment, the SLA apparatus comprises a radiation source 300 (e.g., DLP, laser, electron beam (EB), x-ray, etc. and scanner), a movement control mechanism 302 (e.g., a stepper motor) that moves a build platform 304 vertically up and down within a tank 305 that holds the photopolymer resin 306, and a sweeper 308 (also known as a "recoater" blade) that sweeps horizontally. These elements are used to print a part 310 in the manner previously described. The SLA apparatus is augmented with a foam producing and dispensing mechanism to facilitate production of resin foam at the printer interface, namely, the layer being printed. To this end, the mechanism comprises a foaming or pressure vessel 312, an electromechanical valve 314, and a hose or tube 316. A manifold 318 is attached to the sweeper 308 to evenly distribute the foamed resin across the top layer of the build surface. In particular, and as depicted, the foaming vessel receives liquid resin and a suitable gas (e.g., CO₂, N₂O, etc.). Gas is dissolved in the liquid resin within the foaming vessel (e.g., by shaking, mixing, agitation, etc.) and selectively delivered to the build plate/platform via the hose 316 when the valve 314 is actuated, e.g., by a solenoid or other electromechanical, pneumatic, optical or electronic control device. Typically, the mechanism is under program control using a computer, which may be the same computer used to control the printer. In this embodiment, the mechanism includes a frother 320 (e.g., a mechanical agitator, an ultrasonic device, etc.) to shake or otherwise dissolve the gas within the liquid vessel if needed to produce foam.

[0211] Upon delivery of the resin and gas mixture (directly onto the build plate via the manifold 318), the gas spontaneously evolves out of the liquid mixture (due to the lower pressure) to produce a foam that is radiation-curable. The sweeper 308 spreads the foam evenly onto the plate, and the light engine is then activated to display the appropriate image to cure (solidify) the foam into a layer. Once the layer is formed, the movement control mechanism moves the platform down so that the next layer of the item can be built; the process is then repeated, once again preferably using the foam layer at the print interface. While the preferred technique uses layer-wise additive manufacturing, other manufacturing processes may be used to process the foam to produce the build item, such as, for example, laser holography, wherein two lasers intersect in a tank of foamed resin and cure the resin at that spot.

[0212] The photocurable composition used according to the present invention is preferably used in vat photopolymerization (stereolithography) and photopolymer jetting/printing.

[0213] In addition, the present invention is directed to a method for producing a three-dimensional article, comprising

- a) providing the photocurable composition used according to the present invention,
- b) exposing the photocurable composition to actinic radiation to form a cured cross-section,
- c) repeating steps (a) and (b) to build up a three-dimensional article.

[0214] In a preferred embodiment the method comprises a vat photopolymerization, wherein the photocurable used according to the present invention in step b) is cured directly onto a translated or rotated substrate, and the irradiation is patterned via stereolithography, holography, or digital light projection (DLP).

[0215] In another preferred embodiment the method comprises

- a) applying a layer of the photocurable composition used according to the present invention onto a surface; b) exposing the layer imagewise to actinic radiation to form an imaged cured cross-section;
- c) applying a second layer of the photocurable composition onto the previously exposed imaged cross-section;
- d) exposing the layer from step (c) imagewise to actinic radiation to form an additional imaged cross-section, wherein the radiation causes curing of the second layer in the exposed areas and adhesion to the previously exposed cross-section; and
- e) repeating steps (c) and (d) in order to build up a three-dimensional article.

[0216] Accordingly, the present invention is also directed to a three-dimensional article produced by the method of the present invention, or a three-dimensional article, which is a cured product of the photocurable composition used according to the present invention.

[0217] The three-dimensional article may have an Izod impact strength (unnotched) of greater than 45 kJ/m², especially of greater than 50 kJ/m², very especially of greater than 55 kJ/m². The three-dimensional article may have an E modulus of greater than 1750 MPa, especially of greater than 1950 MPa, very especially of greater than 1950 MPa. The mechanical

properties of the cured compositions (three-dimensional article) can be modified by changing the ratio of 5-methyl-3-vinyl-oxazolidin-2-one and the used oligomers to obtain materials with good mechanical performance, either focusing on high impact strength (Examples 1 to 3) or high E modulus (Example 4).

[0218] The photocurable compositions used according to the present invention may be used in dual cure stereolithography resins suitable for stereolithography techniques (particularly for CLIP). Reference is made to US9,453,142, US2016/0136889, US2016/0137838 and US2016/016077. These resins usually include a first polymerizable system typically polymerized by light (sometimes referred to as "Part A") from which an intermediate object is produced, and also include at least a second polymerizable system ("Part B") which is usually cured after the intermediate object is first formed, and which impart desirable structural and/or tensile properties to the final object. The photocurable compositions used according to the present invention may be comprised by Part A.

[0219] The following examples illustrate the invention without restricting it.

Examples

Viscosity:

[0220] The viscosity of the photocurable compositions was determined at 30 ° C in accordance with DIN EN ISO 3219 using a cone/plate HR-1 Discovery Hybrid Rheometer (TA Instruments) and a cone of 60 mm diameter and an angle of 2° at a shear rate of 100 s⁻¹.present

Preparation of specimen for tensile (DIN ISO 527-1, specimen type 5A) and impact strength tests (DIN ISO 180)

[0221] All specimen were prepared by casting using home-made silicone molds. After filling of the molds the photopolymers were pre-cured (pinning) in a light cabinet equipped with UVA fluorescent tubes (Sylvania blacklight 368, F40W, T12) for 60 seconds at 5.9 mW/cm² irradiance (Gigahertz-Optik X1, sensor UV-3717-4), measued with UV-Control 3CT (UV-technik meyer GmbH). UV curing was performed on both sides of the specimen under a 365 nm UV-LED (Hoenle) in 5 passes (tensile specimen, 2 mm thickness) and 10 passes at 500 mJ/cm².

	Example1	Example 2	Example 3	Example 4
Component	Wt-%	Wt-%	Wt-%	Wt-%
5-methyl-3-vinyl-oxazolidin-2-one	69.50	49.50	39.50	39.50
Laromer® UA 9089 ¹⁾	29.50	49.50	59.50	-
Visiomer® H EMA TM D1 ²⁾	-	-	-	59.50
Omnirad® TPO-L ³⁾	1.00	1.00	1.00	1.00
Total	100.00	100.00	100.00	100.00
Viscosity [mPas] at 30° C/100 s ⁻¹	27	113	259	74
E modulus [MPa]	2000 ± 32	1450 ± 31	1140 ± 32	2730 ± 59
Tensile strength at break [MPa]	47.0 ± 1.2	42.3 ± 2.6	50.8 ± 6.9	84.8 ± 3.3
Elongation at break [%]	29.8 ± 9.2	49.9 ± 12.6	79.8 ± 13.2	7.8 ± 4.3
Izod impact strength (unnotched) [kJ/m ²]	49.6 ± 7.7	57.9 ± 9.9	60.1 ± 13.5	34.1 ± 12.6

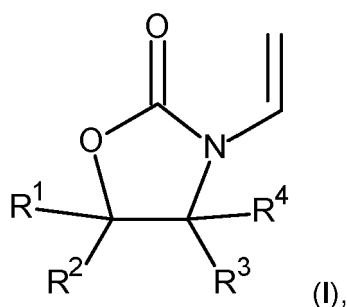
1) BASF, 2) Evonik, 3) IGM Resins.

[0222] As shown in the above Table the mechanical properties of the cured compositions can be modified by changing the ratio of 5-methyl-3-vinyl-oxazolidin-2-one and the used oligomers to obtain materials with good mechanical performance, either focusing on high impact strength (Examples 1 to 3) or high E modulus (Example 4). In addition, the viscosity of the composition in Example 1 is very low which makes it suitable for photopolymer jetting. Low viscous resins are also desired for vat-based printing processes to ensure an efficient recoating step.

Claims

1. Use of a photocurable composition in a photopolymerization 3D printing process, in particular vat photopolymerization, or photopolymer jetting, wherein the photocurable composition, comprises

(A1) a N-vinyloxazolidinone of formula



wherein

R¹, R², R³ and R⁴ are independently of each other a hydrogen atom or an organic group having not more than 10 carbon atoms,

(A2) optionally one, or more second reactive diluents,

(B) one, or more oligomers, and

(C) a photoinitiator (C), wherein the amount of component (A1) is 5 to 70 % by weight based on the amount of components (A1), (A2) and (B), wherein the reactive diluent is a component that contains at least one free radically reactive group that can co-react with components (A1) and (B).

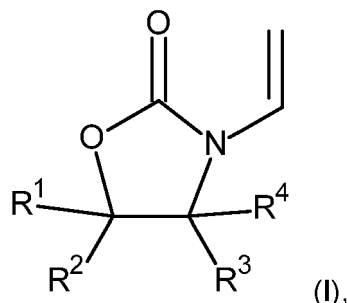
2. A method for producing a three-dimensional article, comprising

a) providing a photocurable composition,

b) exposing the photocurable composition to actinic radiation to form a cured crossection,

c) repeating steps (a) and (b) to build up a three-dimensional article, wherein the photocurable composition, comprises

(A1) a N-vinyloxazolidinone of formula



wherein

R¹, R², R³ and R⁴ are independently of each other a hydrogen atom or an organic group having not more than 10 carbon atoms,

(A2) optionally one, or more second reactive diluents,

(B) one, or more oligomers, and

(C) a photoinitiator (C), wherein the amount of component (A1) is 5 to 70 % by weight based on the amount of components (A1), (A2) and (B), wherein the reactive diluent is a component that contains at least one free radically reactive group that can co-react with components (A1) and (B).

3. The use of the photocurable composition according to claim 1, or the method according to claim 2, wherein the viscosity of the photocurable composition is in the range of 10 to 3000 mPa s, preferably of 10 to 1500 mPa.s at 30 °C, wherein the viscosity of the photocurable composition is determined as described in the description.

4. The use of the photocurable composition according to claim 1, or 3, or the method according to claim 2, or 3, wherein the amount of components (A1) and (A2) is 30 to 70 % by weight, especially 50 to 70 % by weight, very especially 60 to 70 % by weight and the amount of component (B) is 70 to 30 % by weight, especially 50 to 30 % by weight,

very especially 40 to 30 % by weight based on the amount of components (A1), (A2) and (B).

5. The use of the photocurable composition according to claim 1, 3, or 4, or the method according to claim 2, 3, or 4, wherein at least two of R^1 to R^4 in formula I are a hydrogen atom.

6. The use of the photocurable composition according to claim 1, or 3 to 5, or the method according to claim 2, or 3 to 5, wherein the N-vinylloxazolidinone of formula I is selected from a compound, wherein R^1 , R^2 , R^3 and R^4 are a hydrogen atom, a compound, wherein R^1 is a C_1 - C_4 alkyl group, in particular a methyl group, and R^2 , R^3 and R^4 are a hydrogen atom, and a compound, wherein R^1 and R^2 are a hydrogen atom and R^3 and R^4 are a C_1 - C_4 alkyl group, in particular a methyl group, and mixtures thereof.

7. The use of the photocurable composition according to claim 1, or 3 to 6, or the method according to claim 2, or 3 to 6, wherein the oligomer (B) is selected from polyester acrylates, polyether acrylates, epoxy acrylates and urethane acrylates.

8. The use of the photocurable composition according to claim 1, or 3 to 7, or the method according to claim 2, or 3 to 7, wherein the oligomer (B) is obtained by reacting

(B1) a hydroxyalkylacrylate, or hydroxyalkylmethacrylate,

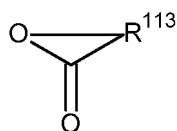
(B2) an aliphatic diisocyanate, an aliphatic polyisocyanate, a cycloaliphatic diisocyanate, a cycloaliphatic polyisocyanate, an aromatic diisocyanate, or an aromatic polyisocyanate, or mixtures thereof,

(B3) a polyester polyol, which is derived from aliphatic dicarboxylic acids and aliphatic diols, and

(B4) optionally a secondary polyol, especially glycerol.

9. The use of the photocurable composition according to claim 8, or the method according to claim 8, wherein component (B1) is selected from 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2- or 3-hydroxypropyl acrylate, 2- or 3-hydroxypropyl methacrylate, 4-hydroxybutyl methacrylate, and 4-hydroxybutyl acrylate, component (B2) is selected from 4,4'-, 2,4'- and/or 2,2'-methylenedicyclohexyl diisocyanate (H12MDI), isophorone diisocyanates (IPDI) and tolylene 2,4- and/or 2,6-diisocyanate (TDI) and the polyester polyol (B3) is derived from adipic acid and ethylene glycol and 1,4-butanediol ((poly(ethylene 1,4-butylene adipate) diol, PEBA).

10. The use of the photocurable composition according to claim 7, or the method according to claim 7, wherein the oligomer (B) is obtained by reacting a polyalkylene glycol with a lactone of formula



(B),

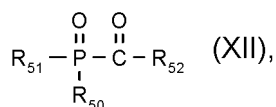
at least one cycloaliphatic or asymmetric aliphatic diisocyanate and an hydroxyalkyl(meth)acrylate, or by reacting a lactone of formula (B) with at least one cycloaliphatic or asymmetric aliphatic diisocyanate and an hydroxyalkyl(meth)acrylate, wherein R^{113} is a divalent alkylene radical having 1 to 12 carbon atoms and which may optionally be substituted by C_1 - C_4 alkyl groups and/or interrupted by one or more oxygen atoms.

11. The use of the photocurable composition according to claim 10, or the method according to claim 10, wherein the oligomer (B) is obtained by reacting s-caprolactone, 4,4'-, 2,4'- and/or 2,2'-methylenedicyclohexyl diisocyanate and hydroxyethylacrylate.

12. The use of the photocurable composition according to claim 7, or the method according to claim 7, wherein the oligomer (B) is obtained by reacting aliphatic, aromatic, or cyclic diisocyanates with hydroxyalkyl(meth)acrylate, especially by reacting trimethylhexamethylene diisocyanate with hydroxyethylmethacrylate.

13. The use of the photocurable composition according to claim 1, or 3 to 12, or the method according to claim 2, or 3 to 12, wherein the photoinitiator (C) is selected from acylphosphine oxide compounds, benzophenone compounds, alpha-aminoketone compounds, phenylglyoxylate compounds, oxime ester compounds, mixtures thereof and mixtures with alpha-hydroxy ketone compounds, or alpha-alkoxyketone compounds.

14. The use of the photocurable composition according to claim 1, or 3 to 12, or the method according to claim 2, or 3 to 12, wherein the photoinitiator (C) is a compound of the formula



wherein

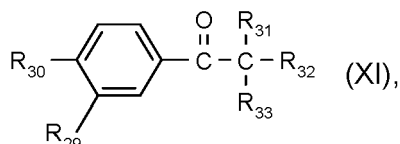
R_{50} is unsubstituted cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenyl; or is cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenyl substituted by one or more halogen, $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_1\text{-C}_{12}$ alkylthio or by $\text{NR}_{53}\text{R}_{54}$;

or R_{50} is unsubstituted $\text{C}_1\text{-C}_{20}$ alkyl or is $\text{C}_1\text{-C}_{20}$ alkyl which is substituted by one or more halogen, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_1\text{-C}_{12}$ alkylthio, $\text{NR}_{53}\text{R}_{54}$ or by $-(\text{CO})\text{-Q-C}_1\text{-C}_{24}$ alkyl;

R_{51} is unsubstituted cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenyl; or is cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenyl substituted by one or more halogen, $\text{C}_1\text{-C}_{12}$ alkyl, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_1\text{-C}_{12}$ alkylthio or by $\text{NR}_{53}\text{R}_{54}$; or R_{51} is $-(\text{CO})\text{R}'_{52}$; or R_{51} is $\text{C}_1\text{-C}_{12}$ alkyl which is unsubstituted or substituted by one or more halogen, $\text{C}_1\text{-C}_{12}$ alkoxy, $\text{C}_1\text{-C}_{12}$ alkylthio, or by $\text{NR}_{53}\text{R}_{54}$;

R_{52} and R'_{52} independently of each other are unsubstituted cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenyl, or are cyclohexyl, cyclopentyl, phenyl, naphthyl or biphenyl substituted by one or more halogen, $\text{C}_1\text{-C}_4$ alkyl or $\text{C}_1\text{-C}_4$ alkoxy; or R_{52} is a 5- or 6-membered heterocyclic ring comprising an S atom or N atom;

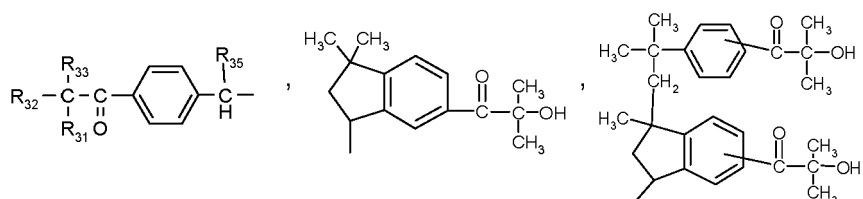
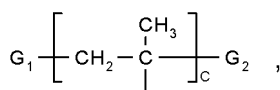
R_{53} and R_{54} independently of one another are hydrogen, unsubstituted $\text{C}_1\text{-C}_{12}$ alkyl or $\text{C}_1\text{-C}_{12}$ alkyl substituted by one or more OH or SH wherein the alkyl chain optionally is interrupted by one to four oxygen atoms; or R_{53} and R_{54} independently of one another are $\text{C}_2\text{-C}_{12}$ -alkenyl, cyclopentyl, cyclohexyl, benzyl or phenyl, or the photoinitiator (C) is a mixture of a compound of the formula (XII) and a compound of the formula

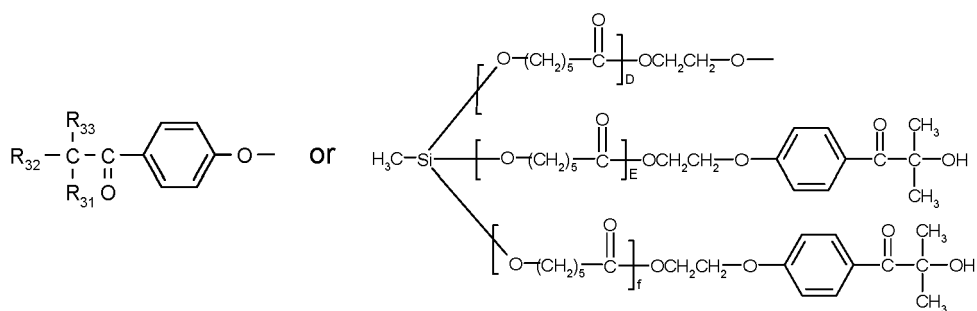


wherein

R_{29} is hydrogen or $\text{C}_1\text{-C}_{18}$ alkoxy;

R_{30} is hydrogen, $\text{C}_1\text{-C}_{18}$ alkyl, $\text{C}_1\text{-C}_{12}$ hydroxyalkyl, $\text{C}_1\text{-C}_{18}$ alkoxy, $\text{OCH}_2\text{CH}_2\text{-OR}_{34}$, morpholino, $\text{S-C}_1\text{-C}_{18}$ alkyl, a group $-\text{HC}=\text{CH}_2$, $-\text{C}(\text{CH}_3)=\text{CH}_2$,



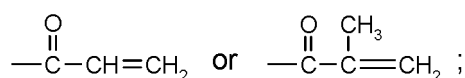


D, E and f are 1-3;

c is 2-10;

G₁ and G₂ independently of one another are end groups of the polymeric structure, preferably hydrogen or methyl;

R₃₄ is hydrogen,



R₃₁ is hydroxy, C₁-C₁₆alkoxy, morpholino, dimethylamino or -O(CH₂CH₂O)_g-C₁-C₁₆alkyl;

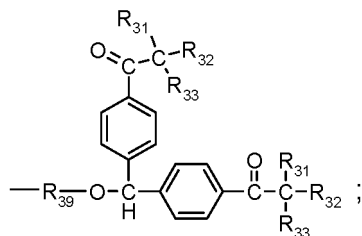
g is 1-20;

R₃₂ and R₃₃ independently of one another are hydrogen, C₁-C₆alkyl, C₁-C₁₆alkoxy or -O(CH₂CH₂O)_g-C₁-C₁₆alkyl; or are unsubstituted phenyl or benzyl; or phenyl or benzyl substituted by C₁-C₁₂-alkyl; or R₃₂ and R₃₃ together with the carbon atom to which they are attached form a cyclohexyl ring;

R₃₅ is hydrogen, OR₃₆ or NR₃₇R₃₈;

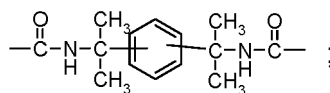
R₃₆ is hydrogen, C₁-C₁₂alkyl which optionally is interrupted by one or more nonconsecutive O-atoms and which uninterrupted or interrupted C₁-C₁₂alkyl optionally is substituted by one or more OH,

or R₃₆ is



R₃₇ and R₃₈ independently of each other are hydrogen or C₁-C₁₂alkyl which is unsubstituted or is substituted by one or more OH;

R₃₉ is C₁-C₁₂alkylene which optionally is interrupted by one or more nonconsecutive O, -(CO)-NH-C₁-C₁₂alkylene-NH-(CO)- or



with the proviso that R₃₁, R₃₂ and R₃₃ not all together are C₁-C₁₆alkoxy or -O(CH₂CH₂O)_g-C₁-C₁₆alkyl, or the photoinitiator is a mixture of different compounds of the formula (XII), or the photoinitiator is a mixture of compounds of the formula (XII) and (XI).

- 15.** The method for producing a three-dimensional article according to claim 2, or 3 to 14, comprising a vat photopolymerization, wherein the photocurable composition in step b) is cured directly onto a translated or rotated substrate, and the irradiation is patterned via stereolithography, holography, or digital light projection (DLP).

16. The method according to claim 2, or 3 to 14, comprising

- a) applying a layer of the photocurable composition onto a surface;
- b) exposing the layer imagewise to actinic radiation to form an imaged cured cross-section;
- c) applying a second layer of the photocurable composition onto the previously exposed imaged cross-section;
- d) exposing the layer from step (c) imagewise to actinic radiation to form an additional imaged cross-section, wherein the radiation causes curing of the second layer in the exposed areas and adhesion to the previously exposed cross-section; and
- e) repeating steps (c) and (d) in order to build up a three-dimensional article.

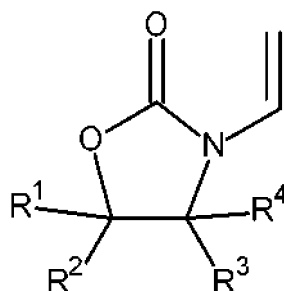
17. A three-dimensional article produced by the method according to claim 2, or 3 to 14.

18. The three-dimensional article according to claim 17 having an Izod impact strength (unnotched) of greater than 45 kJ/m², especially of greater than 50 kJ/m², very especially of greater than 55 kJ/m² and/or an E modulus of greater than 1750 MPa, especially of greater than 1950 MPa.

Patentansprüche

1. Verwendung einer photohärtbaren Zusammensetzung bei einem Photopolymerisations-3D-Druckprozess, insbesondere Vat-Photopolymerisation oder Photopolymer-Jetting, wobei die photohärtbare Zusammensetzung Folgendes umfasst:

(A1) ein N-Vinyloxazolidinon der Formel



(I), wobei

R¹, R², R³ und R⁴ unabhängig voneinander für ein Wasserstoffatom oder eine organische Gruppe mit nicht mehr als 10 Kohlenstoffatomen stehen,

(A2) gegebenenfalls ein oder mehrere zweite reaktive Verdünnungsmittel,

(B) ein oder mehrere Oligomere und

(c) einen Photoinitiator (C), wobei die Menge von Komponente (A1) 5 bis 70 Gew.-%, bezogen auf die Menge der Komponenten (A1), (A2) und (B), beträgt, wobei es sich bei dem reaktiven Verdünnungsmittel um eine Komponente handelt, die mindestens eine radikalisch reaktive Gruppe, die mit den Komponenten (A1) und (B) coreagieren kann, enthält.

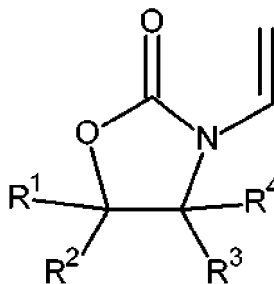
2. Verfahren zur Herstellung eines dreidimensionalen Gegenstands, das Folgendes umfasst:

a) Bereitstellen einer photohärtbaren Zusammensetzung,

b) Belichten der photohärtbaren Zusammensetzung mit aktinischer Strahlung zur Bildung eines gehärteten Querschnitts,

c) Wiederholen der Schritte (a) und (b) zum Aufbauen eines dreidimensionalen Gegenstands, wobei die photohärtbare Zusammensetzung Folgendes umfasst:

(A1) ein N-Vinyloxazolidinon der Formel



(I), wobei

R¹, R², R³ und R⁴ unabhängig voneinander für ein Wasserstoffatom oder eine organische Gruppe mit nicht mehr als 10 Kohlenstoffatomen stehen,

(A2) gegebenenfalls ein oder mehrere zweite reaktive Verdünnungsmittel,

(B) ein oder mehrere Oligomere und

(c) einen Photoinitiator (C), wobei die Menge von Komponente (A1) 5 bis 70 Gew.-%, bezogen auf die Menge der Komponenten (A1), (A2) und (B), beträgt, wobei es sich bei dem reaktiven Verdünnungsmittel um eine Komponente handelt, die mindestens eine radikalisch reaktive Gruppe, die mit den Komponenten (A1) und (B) coreagieren kann, enthält.

3. Verwendung der photohärtbaren Zusammensetzung nach Anspruch 1 oder Verfahren nach Anspruch 2, wobei die Viskosität der photohärtbaren Zusammensetzung im Bereich von 10 bis 3000 mPa s, vorzugsweise von 10 bis 1500 mPa s, bei 30 °C liegt, wobei die Viskosität der photohärtbaren Zusammensetzung wie in der Beschreibung angegeben bestimmt wird.

4. Verwendung der photohärtbaren Zusammensetzung nach Anspruch 1 oder 3 oder Verfahren nach Anspruch 2 oder 3, wobei die Menge der Komponenten (A1) und (A2) 30 bis 70 Gew.-%, insbesondere 50 bis 70 Gew.-%, ganz besonders 60 bis 70 Gew.-%, beträgt und die Menge von Komponente (B) 70 bis 30 Gew.-%, insbesondere 50 bis 30 Gew.-%, ganz besonders 40 bis 30 Gew.-% beträgt, bezogen auf die Menge der Komponenten (A1), (A2) und (B).

5. Verwendung der photohärtbaren Zusammensetzung nach Anspruch 1, 3 oder 4 oder Verfahren nach Anspruch 2, 3 oder 4, wobei mindestens zwei von R¹ bis R⁴ in Formel I für ein Wasserstoffatom stehen.

6. Verwendung der photohärtbaren Zusammensetzung nach Anspruch 1 oder 3 bis 5 oder Verfahren nach Anspruch 2 oder 3 bis 5, wobei das N-Vinylloxazolidinon der Formel I aus einer Verbindung, in der R¹, R², R³ und R⁴ für ein Wasserstoffatom stehen, einer Verbindung, in der R¹ für eine C₁-C₄-Alkylgruppe, insbesondere eine Methylgruppe, steht und R², R³ und R⁴ für ein Wasserstoffatom stehen, und einer Verbindung, in der R¹ und R² für ein Wasserstoffatom stehen und R³ und R⁴ für eine C₁-C₄-Alkylgruppe, insbesondere eine Methylgruppe, stehen, und Mischungen davon ausgewählt ist.

7. Verwendung der photohärtbaren Zusammensetzung nach Anspruch 1 oder 3 bis 6 oder Verfahren nach Anspruch 2 oder 3 bis 6, wobei das Oligomer (B) aus Polyesteracrylaten, Polyetheracrylaten, Epoxyacrylaten und Urethanaacrylaten ausgewählt ist.

8. Verwendung der photohärtbaren Zusammensetzung nach Anspruch 1 oder 3 bis 7 oder Verfahren nach Anspruch 2 oder 3 bis 7, wobei das Oligomer (B) erhalten wird durch Umsetzen von

(B1) einem Hydroxyalkylacrylat oder Hydroxyalkylmethacrylat,

(B2) einem aliphatischen Diisocyanat, einem aliphatischen Polyisocyanat, einem cycloaliphatischen Diisocyanat, einem cycloaliphatischen Polyisocyanat, einem aromatischen Diisocyanat oder einem aromatischen Polyisocyanat oder Mischungen davon,

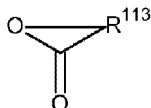
(B3) einem Polyesterpolyol, das von aliphatischen Dicarbonsäuren und aliphatischen Diolen abgeleitet ist, und

(B4) gegebenenfalls einem sekundären Polyol, insbesondere Glycerin.

9. Verwendung der photohärtbaren Zusammensetzung nach Anspruch 8 oder Verfahren nach Anspruch 8, wobei Komponente (B1) aus 2-Hydroxyethylacrylat, 2-Hydroxyethylmethacrylat, 2- oder 3-Hydroxypropylacrylat, 2- oder 3-Hydroxypropylmethacrylat, 4-Hydroxybutylmethacrylat und 4-Hydroxybutylacrylat ausgewählt ist, Komponente

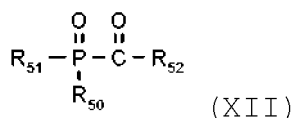
(B2) aus 4,4'-, 2,4'- und/oder 2,2'-Methylen-dicyclohexyldiisocyanat (H12MDI), Isophorondiisocyanaten (IPDI) und Tolylen-2,4- und/oder -2,6-diisocyanat (TDI) ausgewählt ist und das Polyesterpolyol (B3) von Adipinsäure und Ethylenglykol und 1,4-Butandiol abgeleitet ist ((Poly(ethylen-1,4-butylenadipat)diol, PEBA).

10. Verwendung der photohärtbaren Zusammensetzung nach Anspruch 7 oder Verfahren nach Anspruch 7, wobei das Oligomer (B) erhalten wird durch Umsetzen von einem Polyalkylenglykol mit einem Lacton der Formel



(B), mindestens einem cycloaliphatischen oder unsymmetrischen aliphatischen Diisocyanat und einem Hydroxyalkyl(meth)acrylat oder durch Umsetzen eines Lactons der Formel (B) mit mindestens einem cycloaliphatischen oder unsymmetrischen aliphatischen Diisocyanat und einem Hydroxyalkyl(meth)acrylat, wobei R¹¹³ für einen zweiwertigen Alkylrest mit 1 bis 12 Kohlenstoffatomen, der gegebenenfalls durch C₁-C₄-Alkylgruppen substituiert und/oder durch ein oder mehrere Sauerstoffatome unterbrochen sein kann, steht.

11. Verwendung der photohärtbaren Zusammensetzung nach Anspruch 10 oder Verfahren nach Anspruch 10, wobei das Oligomer (B) durch Umsetzen von ε-Caprolacton, 4,4'-, 2,4'- und/oder 2,2'-Methylen-dicyclohexyldiisocyanat und Hydroxyethylacrylat erhalten wird.
12. Verwendung der photohärtbaren Zusammensetzung nach Anspruch 7 oder Verfahren nach Anspruch 7, wobei das Oligomer (B) durch Umsetzen von aliphatischen, aromatischen oder cyclischen Diisocyanaten mit Hydroxyalkyl(meth)acrylat, insbesondere durch Umsetzen von Trimethylhexamethylen-diisocyanat mit Hydroxyethylmethacrylat, erhalten wird.
13. Verwendung der photohärtbaren Zusammensetzung nach Anspruch 1 oder 3 bis 12 oder Verfahren nach Anspruch 2 oder 3 bis 12, wobei der Photoinitiator (C) aus Acylphosphinoxidverbindungen, Benzophenonverbindungen, alpha-Aminoketonverbindungen, Phenylglyoxylatverbindungen, Oximeesterverbindungen, Mischungen davon und Mischungen mit alpha-Hydroxyketonverbindungen oder alpha-Alkoxyketonverbindungen ausgewählt ist.
14. Verwendung der photohärtbaren Zusammensetzung nach Anspruch 1 oder 3 bis 12 oder Verfahren nach Anspruch 2 oder 3 bis 12, wobei es sich bei dem Photoinitiator (C) um eine Verbindung der Formel



handelt, wobei

R₅₀ für unsubstituiertes Cyclohexyl, Cyclopentyl, Phenyl, Naphthyl oder Biphenyl steht oder für Cyclohexyl, Cyclopentyl, Phenyl, Naphthyl oder Biphenyl, das durch ein oder mehrere Halogen, C₁-C₁₂-Alkyl, C₁-C₁₂-Alkoxy, C₁-C₁₂-Alkylthio oder durch NR₅₃R₅₄ substituiert ist, steht; oder R₅₀ für unsubstituiertes C₁-C₂₀-Alkyl oder für C₁-C₂₀-Alkyl, das durch ein oder mehrere Halogen, C₁-C₁₂-Alkoxy, C₁-C₁₂-Alkylthio, NR₅₃R₅₄ oder durch - (CO) -O-C₁-C₂₄-Alkyl substituiert ist, steht;

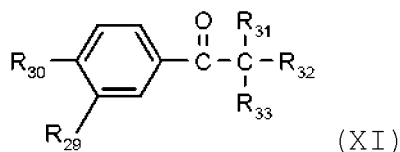
R₅₁ für unsubstituiertes Cyclohexyl, Cyclopentyl, Phenyl, Naphthyl oder Biphenyl steht oder für Cyclohexyl, Cyclopentyl, Phenyl, Naphthyl oder Biphenyl, das durch ein oder mehrere Halogen, C₁-C₁₂-Alkyl, C₁-C₁₂-Alkoxy, C₁-C₁₂-Alkylthio oder durch NR₅₃R₅₄ substituiert ist, steht; oder R₅₁ für -(CO)R'₅₂ steht; oder R₅₁ für C₁-C₁₂-Alkyl, das unsubstituiert oder durch ein oder mehrere Halogen, C₁-C₁₂-Alkoxy, C₁-C₁₂-Alkylthio oder durch NR₅₃R₅₄ substituiert ist, steht;

R₅₂ und R'₅₂ unabhängig voneinander für unsubstituiertes Cyclohexyl, Cyclopentyl, Phenyl, Naphthyl oder Biphenyl stehen oder für Cyclohexyl, Cyclopentyl, Phenyl, Naphthyl oder Biphenyl, das durch ein oder mehrere Halogen, C₁-C₄-Alkyl oder C₁-C₄-Alkoxy substituiert ist, stehen; oder R₅₂ für einen 5- oder 6-gliedrigen heterocyclischen Ring mit einem S-Atomen oder einem N-Atom steht;

R₅₃ und R₅₄ unabhängig voneinander für Wasserstoff, unsubstituiertes C₁-C₁₂-Alkyl oder C₁-C₁₂-Alkyl, das durch ein oder mehrere OH oder SH substituiert ist, stehen, wobei die Alkylkette gegebenenfalls durch ein bis

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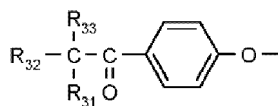
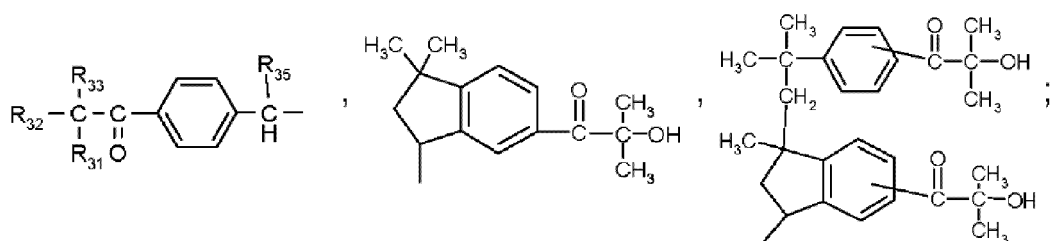
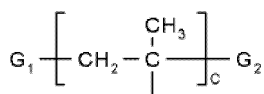
vier Sauerstoffatome unterbrochen ist; oder R_{53} und R_{54} unabhängig voneinander für C_2 - C_{12} -Alkenyl, Cyclopentyl, Cyclohexyl, Benzyl oder Phenyl stehen, oder es sich bei dem Photoinitiator (C) um eine Mischung einer Verbindung der Formel (XII) und einer Verbindung der Formel



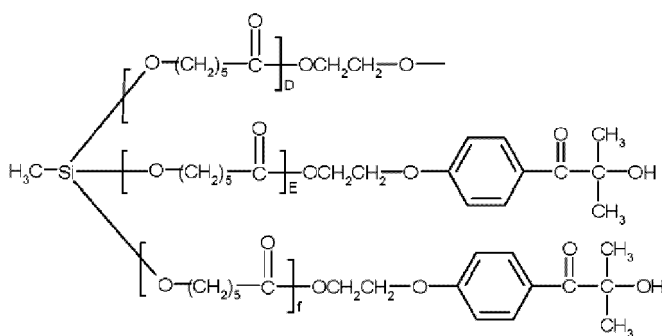
handelt, wobei

R_{29} für Wasserstoff oder C_1 - C_{18} -Alkoxy steht;

R_{30} für Wasserstoff, C_1 - C_{18} -Alkyl, C_1 - C_{12} -Hydroxyalkyl, C_1 - C_{18} -Alkoxy, $\text{OCH}_2\text{CH}_2\text{-OR}_{34}$, Morpholino, S- C_1 - C_{18} -Alkyl, eine Gruppe -HC=CH_2 , $\text{-C(CH}_3\text{)=CH}_2$,



oder



steht;

D, E und f für 1-3 stehen;

c für 2-10 steht;

G_1 und G_2 unabhängig voneinander für Endgruppen der polymeren Struktur, vorzugsweise Wasserstoff oder Methyl, stehen;

R_{34} für Wasserstoff



5

steht;

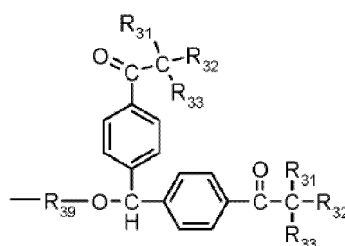
R₃₁ für Hydroxy, C₁-C₁₆-Alkoxy, Morpholino, Dimethylamino oder -O(CH₂CH₂O)_g-C₁-C₁₆-Alkyl steht; g für 1 bis 20 steht;

10 R₃₂ und R₃₃ unabhängig voneinander für Wasserstoff, C₁-C₆-Alkyl, C₁-C₁₆-Alkoxy oder -O (CH₂CH₂O)_g-C₁-C₁₆-Alkyl stehen; oder für unsubstituiertes Phenyl oder Benzyl oder Phenyl oder Benzyl, das durch C₁-C₁₂-Alkyl substituiert ist, stehen; oder R₃₂ und R₃₃ zusammen mit dem Kohlenstoffatom, an das sie gebunden sind, einen Cyclohexylring bilden;

R₃₅ für Wasserstoff, OR₃₆ oder NR₃₇R₃₈ steht;

15 R₃₆ für Wasserstoff, C₁-C₁₂-Alkyl, das gegebenenfalls durch ein oder mehrere nicht aufeinanderfolgende O-Atome unterbrochen ist, wobei das nicht unterbrochene oder unterbrochene C₁-C₁₂-Alkyl gegebenenfalls durch ein oder mehrere OH substituiert ist, steht oder R₃₆ für

20



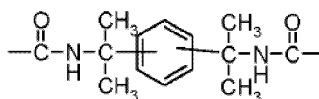
25

steht;

R₃₇ und R₃₈ unabhängig voneinander für Wasserstoff oder C₁-C₁₂-Alkyl, das unsubstituiert oder durch ein oder mehrere OH substituiert ist, stehen;

30 R₃₉ für C₁-C₁₂-Alkylen, das gegebenenfalls durch ein oder mehrere nicht aufeinanderfolgende O unterbrochen ist, - (CO) -NH-C₁-C₁₂-Alkylen-NH- (CO) - oder

35



steht;

40 mit der Maßgabe, dass R₃₁, R₃₂ und R₃₃ nicht alle zusammen für C₁-C₁₆-Alkoxy oder -O (CH₂CH₂O)_g-C₁-C₁₆-Alkyl stehen, oder es sich bei dem Photoinitiator um eine Mischung von verschiedenen Verbindungen der Formel (XII) handelt oder es sich bei dem Photoinitiator um eine Mischung von Verbindungen der Formel (XII) und (XI) handelt.

45 **15.** Verfahren zur Herstellung eines dreidimensionalen Gegenstands nach Anspruch 2 oder 3 bis 14, umfassend eine Vat-Photopolymerisation, wobei die photohärtbare Zusammensetzung in Schritt b) direkt auf einem translatierten oder gedrehten Substrat gehärtet wird und die Bestrahlung mittels Stereolithographie, Holographie oder digitale Lichtprojektion (DLP) strukturiert wird.

50 **16.** Verfahren nach Anspruch 2 oder 3 bis 14, das Folgendes umfasst:

50

- a) Aufbringen einer Schicht der photohärtbaren Zusammensetzung auf eine Oberfläche;
- b) bildmäßiges Belichten der Schicht mit aktinischer Strahlung zur Bildung eines bebilderten gehärteten Querschnitts;
- c) Aufbringen einer zweiten Schicht der photohärtbaren Zusammensetzung auf den vorher belichteten bebilderten Querschnitt;
- 55 d) bildmäßiges Belichten der Schicht aus Schritt (c) mit aktinischer Strahlung zur Bildung eines zusätzlichen bebilderten Querschnitts, wobei die Strahlung das Härten der zweiten Schicht in den belichteten Bereichen und Haftung auf dem vorher belichteten Querschnitt bewirkt; und

e) Wiederholen der Schritte (c) und (d) zum Aufbauen eines dreidimensionalen Gegenstands.

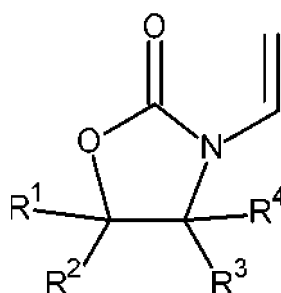
17. Dreidimensionaler Gegenstand, hergestellt durch das Verfahren nach Anspruch 2 oder 3 bis 14.

18. Dreidimensionaler Gegenstand nach Anspruch 17 mit einer IZOD-Schlagzähigkeit (ungekerbt) von mehr als 45 kJ/m², speziell von mehr als 50 kJ/m², ganz speziell von mehr als 55 kJ/m², und/oder einem E-Modul von mehr als 1750 MPa, speziell von mehr als 1950 MPa.

Revendications

1. Utilisation d'une composition photodurcissable dans un procédé d'impression 3D par photopolymérisation, en particulier la photopolymérisation en cuve, ou jet de photopolymère, dans laquelle la composition photodurcissable comprend

(A1) une N-vinyloxazolidinone de formule



(I), dans laquelle

R¹, R², R³ et R⁴ sont indépendamment les uns des autres un atome d'hydrogène ou un groupe organique n'ayant pas plus de 10 atomes de carbone,

(A2) éventuellement un ou plusieurs deuxièmes diluants réactifs,

(B) un ou plusieurs oligomères, et

(c) un photoinitiateur (C), dans laquelle la quantité de composant (A1) est de 5 à 70 % en poids sur la base de la quantité de composants (A1), (A2) et (B), dans laquelle le diluant réactif est un composant qui contient au moins un groupe réactif par voie radicalaire libre qui peut co-réagir avec les composants (A1) et (B).

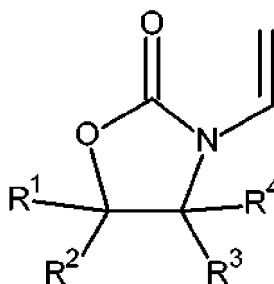
2. Procédé de production d'un article tridimensionnel, comprenant

a) la fourniture d'une composition photodurcissable,

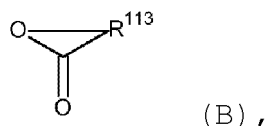
b) l'exposition de la composition photodurcissable à un rayonnement actinique pour former une section transversale durcie,

c) la répétition des étapes (a) et (b) pour construire un article tridimensionnel, dans lequel la composition photodurcissable comprend

(A1) une N-vinyloxazolidinone de formule



- (I), dans lequel
 R^1 , R^2 , R^3 et R^4 sont indépendamment les uns des autres un atome d'hydrogène ou un groupe organique n'ayant pas plus de 10 atomes de carbone,
 (A2) éventuellement un ou plusieurs deuxièmes diluants réactifs,
 (B) un ou plusieurs oligomères, et
 (c) un photoinitiateur (C), dans lequel la quantité de composant (A1) est de 5 à 70 % en poids sur la base de la quantité de composants (A1), (A2) et (B), dans lequel le diluant réactif est un composant qui contient au moins un groupe réactif par voie radicalaire libre qui peut co-réagir avec les composants (A1) et (B).
3. Utilisation de la composition photodurcissable selon la revendication 1, ou procédé selon la revendication 2, dans laquelle/lequel la viscosité de la composition photodurcissable est dans la plage de 10 à 3 000 mPa.s, de préférence de 10 à 1 500 mPa.s à 30 °C, dans laquelle/lequel la viscosité de la composition photodurcissable est déterminée comme décrit dans la description.
4. Utilisation de la composition photodurcissable selon la revendication 1, ou 3, ou procédé selon la revendication 2, ou 3, dans laquelle/lequel la quantité de composants (A1) et (A2) est de 30 à 70 % en poids, notamment de 50 à 70 % en poids, très particulièrement de 60 à 70 % en poids et la quantité de composant (B) est de 70 à 30 % en poids, notamment de 50 à 30 % en poids, très particulièrement de 40 à 30 % en poids sur la base de la quantité de composants (A1), (A2) et (B).
5. Utilisation de la composition photodurcissable selon la revendication 1, 3 ou 4, ou procédé selon la revendication 2, 3 ou 4, dans laquelle/lequel au moins deux parmi R^1 à R^4 dans la formule I sont un atome d'hydrogène.
6. Utilisation de la composition photodurcissable selon la revendication 1, ou 3 à 5, ou procédé selon la revendication 2, ou 3 à 5, dans laquelle/lequel la N-vinylloxazolidinone de formule I est choisie parmi un composé, dans laquelle/lequel R^1 , R^2 , R^3 et R^4 sont un atome d'hydrogène, un composé, dans laquelle/lequel R^1 est un groupe C_1 - C_4 alkyle, en particulier un groupe méthyle, et R^2 , R^3 et R^4 sont un atome d'hydrogène, et un composé, dans laquelle/lequel R^1 et R^2 sont un atome d'hydrogène et R^3 et R^4 sont un groupe C_1 - C_4 alkyle, en particulier un groupe méthyle, et des mélanges correspondants.
7. Utilisation de la composition photodurcissable selon la revendication 1, ou 3 à 6, ou procédé selon la revendication 2, ou 3 à 6, dans laquelle/lequel l'oligomère (B) est choisi parmi des acrylates de polyester, des acrylates de polyéther, des acrylates d'époxy et des acrylates d'uréthane.
8. Utilisation de la composition photodurcissable selon la revendication 1, ou 3 à 7, ou procédé selon la revendication 2, ou 3 à 7, dans laquelle/lequel l'oligomère (B) est obtenu par mise en réaction
- (B1) d'un acrylate d'hydroxyalkyle ou méthacrylate d'hydroxyalkyle,
 (B2) d'un diisocyanate aliphatique, d'un polyisocyanate aliphatique, d'un diisocyanate cycloaliphatique, d'un polyisocyanate cycloaliphatique, d'un diisocyanate aromatique ou d'un polyisocyanate aromatique ou des mélanges correspondants,
 (B3) d'un polyesterpolyol qui est issu d'acides dicarboxyliques aliphatiques et de diols aliphatiques, et
 (B4) éventuellement un polyol secondaire, notamment le glycérol.
9. Utilisation de la composition photodurcissable selon la revendication 8, ou procédé selon la revendication 8, dans laquelle/lequel le composant (B1) est choisi parmi l'acrylate de 2-hydroxyéthyle, le méthacrylate de 2-hydroxyéthyle, l'acrylate de 2- ou 3-hydroxypropyle, le méthacrylate de 2- ou 3-hydroxypropyle, le méthacrylate de 4-hydroxybutyle et l'acrylate de 4-hydroxybutyle, le composant (B2) est choisi parmi le 4,4'-, 2,4'- et/ou 2,2'-diisocyanate de méthylènedicyclohexyle (H12MDI), les diisocyanates d'isophorone (IPDI) et le 2,4- et/ou 2,6-diisocyanate de tolylène (TDI) et le polyester polyol (B3) est issu d'acide adipique et d'éthylène glycol et de 1,4-butanediol ((poly(éthylène-adipate de 1,4-butylène)diol, PEBA) .
10. Utilisation de la composition photodurcissable selon la revendication 7, ou procédé selon la revendication 7, dans laquelle/lequel l'oligomère (B) est obtenu par mise en réaction d'un polyalkylèneglycol avec une lactone de formule



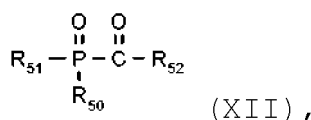
au moins un diisocyanate aliphatique asymétrique ou cycloaliphatique et un (méth) acrylate d'hydroxyalkyle, ou par mise en réaction d'une lactone de formule (B) avec au moins un diisocyanate aliphatique asymétrique ou cycloaliphatique et un (méth)acrylate d'hydroxyalkyle, dans laquelle/lequel R^{113} est un radical alkylène divalent ayant 1 à 12 atomes de carbone et qui peut éventuellement être substitué par des groupes C_1 - C_4 alkyle et/ou interrompu par un ou plusieurs atomes d'oxygène.

11. Utilisation de la composition photodurcissable selon la revendication 10, ou procédé selon la revendication 10, dans laquelle/lequel l'oligomère (B) est obtenu par mise en réaction de ϵ -caprolactone, de 4,4'-, 2,4'- et/ou 2,2'-diisocyanate de méthylènedicyclohexyle et d'acrylate d'hydroxyéthyle.

12. Utilisation de la composition photodurcissable selon la revendication 7, ou procédé selon la revendication 7, dans laquelle/lequel l'oligomère (B) est obtenu par mise en réaction de diisocyanates aliphatiques, aromatiques ou cycliques avec un (méth)acrylate d'hydroxyalkyle, notamment par mise en réaction de diisocyanate de triméthylhexaméthylène avec le méthacrylate d'hydroxyéthyle.

13. Utilisation de la composition photodurcissable selon la revendication 1, ou 3 à 12, ou procédé selon la revendication 2, ou 3 à 12, dans laquelle/lequel le photoinitiateur (C) est choisi parmi des composés d'oxyde d'acylphosphine, des composés de benzophénone, des composés d'alpha-aminocétone, des composés de phénylglyoxylate, des composés d'ester d'oxime, des mélanges correspondants et des mélanges avec des composés d'alpha-hydroxycétone ou des composés d'alpha-alcoxycétone.

14. Utilisation de la composition photodurcissable selon la revendication 1, ou 3 à 12, ou procédé selon la revendication 2, ou 3 à 12, dans laquelle/lequel le photoinitiateur (C) est un composé de la formule



dans laquelle/lequel

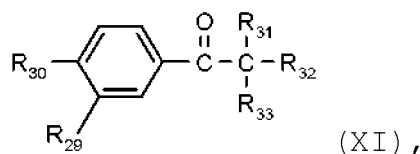
R_{50} est cyclohexyle, cyclopentyle, phényle, naphtyle ou biphenyle non substitué ; ou est cyclohexyle, cyclopentyle, phényle, naphtyle ou biphenyle substitué par un ou plusieurs halogènes, C_1 - C_{12} alkyle, C_1 - C_{12} alcoxy, C_1 - C_{12} alkylthio ou par $NR_{53}R_{54}$;

ou R_{50} est C_1 - C_{20} alkyle non substitué ou est C_1 - C_{20} alkyle qui est substitué par un ou plusieurs halogènes, C_1 - C_{12} alcoxy, C_1 - C_{12} alkylthio, $NR_{53}R_{54}$ ou par $-(CO)-O-C_1-C_{24}$ alkyle ;

R_{51} est cyclohexyle, cyclopentyle, phényle, naphtyle ou biphenyle non substitué ; ou est cyclohexyle, cyclopentyle, phényle, naphtyle ou biphenyle substitué par un ou plusieurs halogènes, C_1 - C_{12} alkyle, C_1 - C_{12} alcoxy, C_1 - C_{12} alkylthio ou par $NR_{53}R_{54}$; ou R_{51} est $-(CO)R'_{52}$; ou R_{51} est C_1 - C_{12} alkyle qui est non substitué ou substitué par un ou plusieurs halogènes, C_1 - C_{12} alcoxy, C_1 - C_{12} alkylthio, ou par $NR_{53}R_{54}$;

R_{52} et R'_{52} indépendamment l'un de l'autre sont cyclohexyle, cyclopentyle, phényle, naphtyle ou biphenyle non substitué, ou sont cyclohexyle, cyclopentyle, phényle, naphtyle ou biphenyle substitué par un ou plusieurs halogènes, C_1 - C_4 alkyle ou C_1 - C_4 alcoxy ; ou R_{52} est un cycle hétérocyclique à 5 ou 6 chaînons comprenant un atome de S ou un atome de N ;

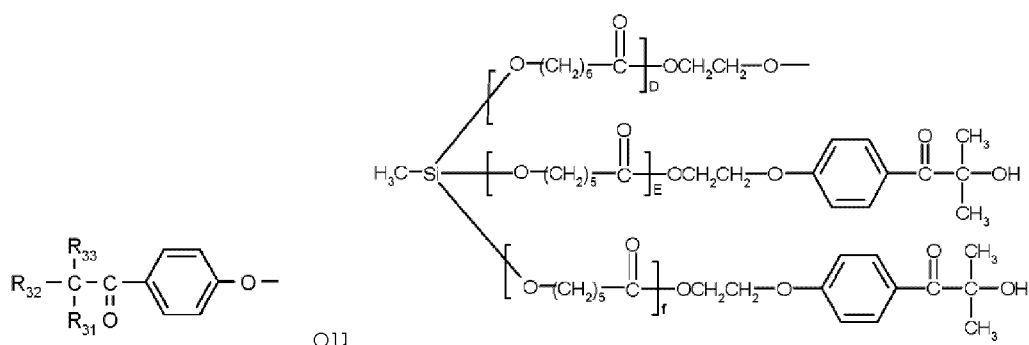
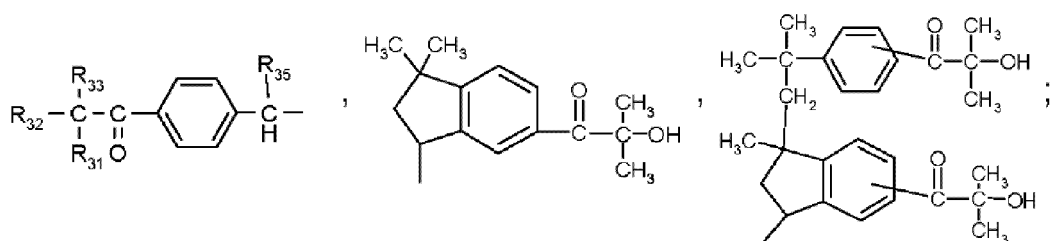
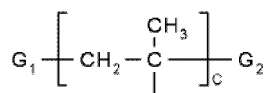
R_{53} et R_{54} indépendamment l'un de l'autre sont hydrogène, C_1 - C_{12} alkyle non substitué ou C_1 - C_{12} alkyle substitué par un ou plusieurs OH ou SH dans laquelle/lequel la chaîne alkyle est éventuellement interrompue par un à quatre atomes d'oxygène ; ou R_{53} et R_{54} indépendamment l'un de l'autre sont C_2 - C_{12} alcényle, cyclopentyle, cyclohexyle, benzyle ou phényle, ou le photoinitiateur (C) est un mélange d'un composé de la formule (XII) et d'un composé de la formule



dans laquelle/lequel

R_{29} est hydrogène ou $\text{C}_1\text{-C}_{18}$ alcoxy ;

R_{30} est hydrogène, $\text{C}_1\text{-C}_{18}$ alkyle, $\text{C}_1\text{-C}_{12}$ hydroxyalkyle, $\text{C}_1\text{-C}_{18}$ alcoxy, $\text{OCH}_2\text{CH}_2\text{-OR}_{34}$, morpholino, $\text{S-C}_1\text{-C}_{18}$ alkyle, un groupe -HC=CH_2 , $\text{-C(CH}_3\text{)=CH}_2$,

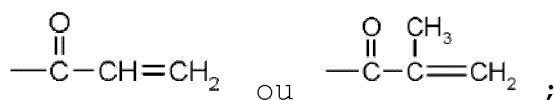


D, E et f sont 1-3 ;

c est 2-10 ;

G_1 et G_2 indépendamment l'un de l'autre sont des groupes terminaux de la structure polymérique, préférentiellement hydrogène ou méthyle ;

R_{34} est hydrogène



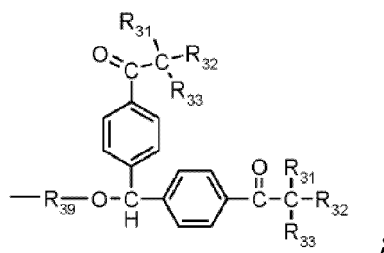
R_{31} est hydroxy, $\text{C}_1\text{-C}_{16}$ alcoxy, morpholino, diméthylamino ou $\text{-O(CH}_2\text{CH}_2\text{O)}_g\text{-C}_1\text{-C}_{16}$ alkyle ;
g est 1-20 ;

R_{32} et R_{33} indépendamment l'un de l'autre sont hydrogène, $\text{C}_1\text{-C}_6$ alkyle, $\text{C}_1\text{-C}_{16}$ alcoxy ou $\text{-O(CH}_2\text{CH}_2\text{O)}_g\text{-C}_1\text{-C}_{16}$ alkyle ; ou sont phényle ou benzyle non substitué ; ou phényle ou benzyle substitué par $\text{C}_1\text{-C}_{12}$ alkyle ; ou R_{32} et R_{33} conjointement avec l'atome de carbone auquel ils sont fixés forment un cycle cyclohexyle ;

R_{35} est hydrogène, OR_{36} ou $\text{NR}_{37}\text{R}_{38}$;

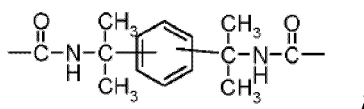
R_{36} est hydrogène, $\text{C}_1\text{-C}_{12}$ alkyle qui est éventuellement interrompu par un ou plusieurs atomes de O non consécutifs et lequel $\text{C}_1\text{-C}_{12}$ alkyle ininterrompu ou interrompu est éventuellement substitué par un ou

plusieurs OH,
ou R₃₆ est



R₃₇ et R₃₈ indépendamment l'un de l'autre sont hydrogène ou C₁-C₁₂alkyle qui est non substitué ou est substitué par un ou plusieurs OH ;

R₃₉ est C₁-C₁₂alkylène qui est éventuellement interrompu par un ou plusieurs O non consécutifs, -(CO)-NH-C₁-C₁₂alkylène-NH- (CO) - ou



à condition que R₃₁, R₃₂ et R₃₃ ne soient pas tous ensemble C₁-C₁₆alcoxy ou -O(CH₂CH₂O)_g-C₁-C₁₆alkyle, ou le photoinitiateur est un mélange de différents composés de la formule (XII), ou le photoinitiateur est un mélange de composés de la formule (XII) et (XI).

15. Procédé de production d'un article tridimensionnel selon la revendication 2, ou 3 à 14, comprenant une photopolymérisation en cuve, dans lequel la composition photodurcissable à l'étape b) est durcie directement sur un substrat en translation ou en rotation, et l'irradiation est structurée par stéréolithographie, holographie ou projection de lumière numérique (DLP).

16. Procédé selon la revendication 2, ou 3 à 14, comprenant

- une application d'une couche de la composition photodurcissable sur une surface ;
- une exposition de la couche par image à un rayonnement actinique pour former une section transversale durcie à image ;
- une application d'une deuxième couche de la composition photodurcissable sur la section transversale à image exposée précédemment ;
- une exposition de la couche de l'étape (c) à un rayonnement actinique pour former une section transversale à image supplémentaire, dans lequel le rayonnement entraîne le durcissement de la deuxième couche dans les zones exposées et l'adhérence à la section transversale précédemment exposée ; et
- la répétition des étapes (c) et (d) afin de construire un article tridimensionnel.

17. Article tridimensionnel produit par le procédé selon la revendication 2, ou 3 à 14.

18. Article tridimensionnel selon la revendication 17 ayant une résistance à l'impact Izod (sans encoche) supérieure à 45 kJ/m², notamment supérieure à 50 kJ/m², très particulièrement supérieure à 55 kJ/m² et/ou un module E supérieur à 1 750 MPa, notamment supérieur à 1 950 MPa.

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